the normal description of the octahedral modes, as given in Table III, is reasonably accurate. The deviation from a purely distorted ion model is due to the relatively short intermolecular fluorine–fluorine distances and the consequent necessity of including fluorine–fluorine interaction terms. These A_2MF_6 complexes, therefore, do not constitute a particularly good system for studying the application of the UBFF to a distorted octahedron in isolation. However, it should be emphasized that if the experimental symmetry assignments were disregarded, then an apparent fit to the observed frequencies could have been obtained *without* the inclusion of lattice interactions. This latter point illustrates the dangers of normal-coordinate analysis of solid-state systems without prior knowledge as to the symmetry species of the observed bands.

The normal coordinates of the lattice modes are shown diagrammatically in Figure 4. The higher frequency E_g mode can be assigned to the rotatory lattice mode although there is some translational motion of the cations. The frequency of this mode cannot be reproduced without the inclusion of the fluorine–fluorine interaction term, but in K_2TiF_6 it occurs 21 cm^{-1} below the observed value. This, again, could be explained on the basis of a mistaken TiF_6^{2-} geometry. Since mixing between internal and lattice modes is minimal, the translatory lattice modes can be simply described as an out-of-phase vibration of the ions in the xy plane (E modes) or along the z axis (A modes). However the agreement between the observed and calculated frequencies for the translatory lattice modes is, in general, poor even for Rb_2ZrF_6 and Cs_2HfF_6. The E modes are observed at higher frequency than the A modes whereas they are calculated in the reverse order. Part of the explanation for this might lie in the restriction which was imposed on the cation–fluorine interaction constants, but if these are allowed to vary randomly, then refined values are obtained which are unrelated to the ion–ion distances involved. This may be another indication of a slight error in positioning of the ions in the crystal structure analysis since a change in the position of the alkali metal ion along the z axis could easily reverse the calculated frequencies of the E and A modes. However, by giving the three types of cation–fluorine interaction a single value, any structural inaccuracies of this type would not be apparent. Alternatively, it should be emphasized that the force field may simply be inadequate to describe lattice interactions fully although it is difficult to envisage, considering other work in this field, how any improvement could be made.

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Registry No. K_2TiF_6, 16919-27-0; Rb_2ZrF_6, 16962-10-0; Cs_2HfF_6, 16919-32-7; PtF_6, 13693-05-5; WF_6, 7783-82-6.

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Analysis of the Vibrational Spectra of μ-Oxo-Bridged Complexes[1]

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Analysis of the Raman spectra of several representative linear μ-oxo-bridged complexes reveals that the symmetrical metal–oxygen–metal stretching vibration is significantly lower than the corresponding vibration observed in bent μ-oxo-bridged complexes. The utility of this result as it relates to the study of the μ-oxo-decahalo ions $[Ru_2OCl_{10}]^{4-}$, $[Os_2OCl_{10}]^{4-}$, $[W_2OCl_{10}]^{4-}$, and other μ-oxo-bridged complexes is discussed.

Infrared spectroscopy is well established as a technique of general usefulness in structural investigations of oxometal complexes.[2–5] These compounds frequently display characteristic absorptions in regions of the infrared spectrum that are readily accessible to general instrumentation. However, characterization of the important class of oxometal complexes which contain ir-inactive metal–oxygen vibrations and/or metal–oxygen vibrations which occur in the low-energy region of the vibrational spectrum and, consequently, cannot be investigated with routine infrared instrumentation remains a difficult problem. Although single-crystal x-ray diffraction studies are being carried out on an increasing number of complexes, development of an alternative spectroscopic approach to the study of this family of complexes would constitute a useful addition to the range of techniques applicable to the examination of these materials.

The work reported in this paper was initiated in the hope that Raman spectroscopy could be applied to the structural characterization of certain oxometal complexes. Here we wish to report the results of an investigation stressing the qualitative

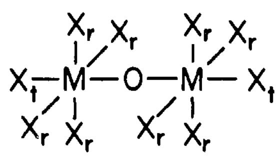

Figure 1. Idealized structure showing the D_{4h} symmetry of the $[M_2OX_{10}]^{4-}$ ion (M = Ru, Os, W; X = halogen).

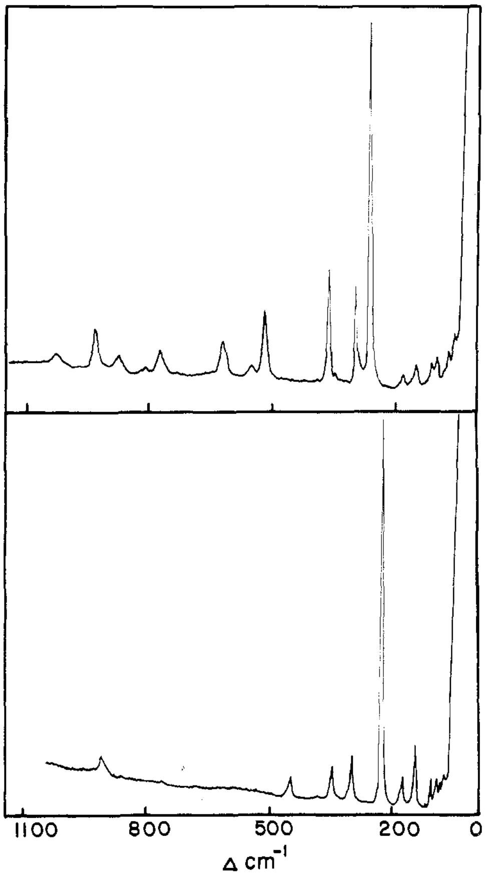

Figure 2. Solid-state Raman spectra of tetracesium μ-oxo-decachlorodiruthenium(IV) (upper) and tetrapotassium μ-oxo-decachlorodiosmium(IV) (lower) recorded, respectively, using 5145- and 4880-Å exciting radiation.

Table I. Selected Solid-State Raman and Infrared Frequencies (cm^{-1}) Observed for $[M_2OX_{10}]^{4-}$ [a]

Raman	Infrared	Assignment
	$K_4[Ru_2OCl_{10}]$	
1545 vw[b]		$6\nu_1$
1285 w		$5\nu_1$
1030 w		$4\nu_1$
930 w-m		
	888 w	ν_6 (A_{2u}), ν_{as}(Ru-O-Ru)
875 w		$2\nu_1 + \nu_5$
810 vw		$2\nu_1 + \nu_2$
774 w-m		$3\nu_1$
619 vw		$\nu_1 + \nu_5$
550 vw		$\nu_1 + \nu_2$
518 m		$2\nu_1$
360 m		ν_5, ν(Ru-Cl$_r$)
	334 sh	ν_4, ν(Ru-Cl)
	328 vs	ν_3, ν(Ru-Cl)
294 m		ν_2, ν(Ru-Cl$_t$)
259 (256; $\rho_1 = 0.35$)[e] vs		ν_1 (A_{1g}), ν_s(Ru-O-Ru)
	$Cs_4[Ru_2OCl_{10}]$	
	887 vw	ν_6 (A_{2u}), ν_{as}(Ru-O-Ru)
756 w[b]		$3\nu_1$
601 m		$\nu_1 + \nu_5$
544 w		$\nu_1 + \nu_2$
504 m		$2\nu_1$
351 m		ν_5, ν(Ru-Cl$_r$)
	324 vs	ν_4, ν(Ru-Cl)
	309 sh	ν_3, ν(Ru-Cl)
290 m		ν_2, ν(Ru-Cl$_t$)
252 vs		ν_1, (A_{1g}), ν_s(Ru-O-Ru)
	$Cs_4[Ru_2OBr_{10}]$	
243 vs		ν_1 (A_{1g}), ν_s(Ru-O-Ru)
199 m-s		ν_5, ν(Ru-Br$_r$)
154 m-s		ν_2, ν(Ru-Br$_t$)
	$Cs_4[Os_2OCl_{10}]$	
857[c]		*d*
	852 vw	ν_6 (A_{2u}), ν_{as}(Os-O-Os)
675 w	562 w-m	$3\nu_1$
555 w		$\nu_1 + \nu_5$
450 w-m		$2\nu_1$
332 w		ν_5, ν(Os-Cl$_r$)
	311 vs	ν_4, ν(Os-Cl)
	304 vs	ν_3, ν(Os-Cl)
285 w		ν_2, ν(Os-Cl$_t$)
225 (229; $\rho_1 = 0.34$)[e] vs		ν_1 (A_{1g}), ν_s(Os-O-Os)
	$K_4[Os_2OCl_{10}]$	
911 w[c]		*d*
	821 w	ν_6 (A_{2u}), ν_{as}(Os-O-Os)
	583 m	
455 w		$2\nu_1$
350 m		ν_5, ν(Os-Cl$_r$)
	329 sh	ν_4, ν(Os-Cl)
	313 vs	ν_3, ν(Os-Cl)
301 m		ν_2, ν(Os-Cl$_t$)
229 vs		ν_1 (A_{1g}), ν_s(Os-O-Os)
179 m		
147 m		

[a] Qualitative intensities: vs, very strong; s, strong; m, medium; w, weak; vw, very weak; sh, shoulder; br, broad. [b] These Raman values were recorded using 5145-Å exciting radiation. [c] These Raman values were recorded using 4880-Å exciting radiation. [d] Impurity [possibly ν(M=O)]. [e] In general, salts of $M_2OX_{10}{}^{n-}$ (M = Ru, Os, W; X = Cl, Br) have very limited solubility and/or stability in solution. These values represent the frequency and depolarization ratio observed for a saturated solution (~10^{-2}–$10^{-3}M$) in 6 *N* HCl.

utility of Raman spectroscopy as a technique for the study of a particular class of oxometal complexes, viz., those containing a single metal–oxygen–metal unit. The reasons for emphasizing this class of compounds are twofold. First, group theory predicts and other studies sustain[2-5] two metal–oxygen–metal stretching vibrations in such molecules: a higher frequency asymmetric stretch and a lower frequency symmetric stretch. The former is observed for and is characteristic of both linear and bent μ-oxo-bridged systems. The latter mode, although potentially the more informative because its position is believed to reflect more directly the metal–oxygen–metal angle,[4] remains ill characterized. Second, linear μ-oxo-bridged complexes have generated considerable interest, initially because of their frequent antiferromagnetic behavior[6] and more recently because of their potential biological importance.[7]

Results

The linear μ-oxo-decahalo ions $[M_2OX_{10}]^{4-}$ (M = Ru, Os; X = Cl) are among the simplest, purportedly best characterized, and, therefore, most attractive compounds for initial study. Several lines of evidence (vide infra) suggest that the idealized structure shown in Figure 1 (point group D_{4h}) is common to all of these ions. Group theory considerations predict four Raman-active (2 A_{1g}, B_{1g}, and E_g) as well as three ir-active (2 A_{2u} and E_u) metal–halogen stretching modes in addition to the symmetric (Raman active) and asymmetric (ir active) metal–oxygen–metal stretching vibrations.

$[Ru_2OX_{10}]^{4-}$. An early single-crystal x-ray study has established[8] the general geometry shown in Figure 1 for the $[Ru_2OCl_{10}]^{4-}$ ion. It seems reasonable to assume a similar geometry for $[Ru_2OBr_{10}]^{4-}$. The Raman spectrum of $Cs_4[Ru_2OCl_{10}]$ is seen in Figure 2. It is characterized by an intense band at 259 cm^{-1} which we assign as the symmetric

(A_{1g}) Ru–O–Ru stretch.[9] This assignment is sustained by depolarization studies. A depolarization ratio $\rho_l = 0.35$ was observed with the near-resonance 5145-Å exciting line.[10] Further support for this conclusion is provided by the fact that the bromo analogue, $Cs_4[Ru_2OBr_{10}]$, displays a similarly intense band at 243 cm^{-1}. The spectral data for these compounds and the related complex $K_4[Ru_2OCl_{10}]$ are collected in Table I.

Several additional features are apparent from a comparison of these results. First, two bands of medium to weak intensity appear at 360 and 294 cm^{-1} in the spectrum of the $Cs_4[Ru_2OCl_{10}]$ and at 199 and 154 cm^{-1} in the spectrum of the bromo analogue $Cs_4[Ru_2OBr_{10}]$. These values fall in the appropriate ranges for metal–chlorine and metal–bromine vibrations[13] and accordingly are assigned as arising principally from radial halogen–ruthenium and terminal halogen–ruthenium stretching frequencies, respectively.[14] Second, the asymmetric metal–oxygen–metal stretching frequency, ν_{as} (Ru–O–Ru), observed in the infrared spectrum of $Cs_4[Ru_2OCl_{10}]$ at ~888 cm^{-1} is absent in the Raman spectrum. Third, the remaining higher energy bands can be assigned as overtone and combination bands. Fourth, a comparison of the spectra of $K_4[Ru_2OCl_{10}]$ and $Cs_4[Ru_2OCl_{10}]$ shows no significant differences and suggests that, at least within these limited examples, the nature of the cation does not substantially influence spectral parameters. Finally, because we are dealing with resonance Raman scattering (vide infra), it is not surprising that the observed vibrational spectrum is incomplete, since only those modes are enhanced which couple to the electronic transition with which the scattered radiation is in resonance.

$[Os_2OCl_{10}]^{4-}$. The isostructural relation between the ions $[Ru_2OCl_{10}]^{4-}$ and $[Os_2OCl_{10}]^{4-}$ was recently demonstrated by an x-ray crystallographic study[15] which, in addition, revealed a significant difference between the terminal and radial chlorine–osmium bond distance (2.433 Å vs. 2.370 Å, respectively). The Raman spectrum of $Cs_4[Os_2OCl_{10}]$ is seen in Figure 2. It reveals an intense band at 225 cm^{-1}, assigned as the symmetric Os–O–Os stretching vibration, an assignment supported by the solution depolarization ratio, $\rho = 0.34$, observed with the near-resonance 4880-Å exciting line. Two weaker bands appear at 351 and 290 cm^{-1} and are assigned respectively as $\nu(Os–Cl_r)$ and $\nu(Os–Cl_t)$. Several overtone and combination bands appear at higher frequencies. These data are also collected in Table I.[16]

A comparison of the data in Table I is informative. It reveals that substitution of bromine for chlorine results in a relatively small shift (~16 cm^{-1}) in ν(M–O–M). A greater shift (~34 cm^{-1}) occurs when ruthenium is replaced by osmium. These observations are consistent with the influence which remote and proximal changes in reduced mass can be expected to have on the stretching frequency of the linear M–O–M unit, which, to a first approximation, can be considered as a simple triatomic system.

$[W_2OCl_{10}]^{4-}$. The reduction of dipotassium tungstate(VI) by tin in concentrated hydrochloric acid was reported by Olsson to yield a substance which he formulated as $K_2[W(OH)Cl_5]$.[17] On the basis of infrared and magnetic studies, Colton and Rose[18] reformulated this material as tetrapotassium μ-oxo-decachloroditungstate(IV), $K_4[W_2OCl_{10}]$. König[19] studied this substance and concluded, based on infrared data, that the tungsten–oxygen–tungsten unit was *bent* with an angle of ~140°.

We have repeated the preparation of this substance. The results of our investigation of this material are in general agreement with those reported by Colton;[18] in particular we concur that this material contains the μ-oxo-decachloroditungstate ion $[W_2OCl_{10}]^{4-}$, howbeit extensively contaminated. Continued reduction of this material with tin in concentrated hydrochloric acid affords the green enneachloroditungstate(III) ion, $[W_2Cl_9]^{3-}$, which is the established end product resulting from the reduction of dipotassium tungstate with tin in concentrated hydrochloric acid.[20,21] This conclusion explains, among other things, the conflicting color and behavior reported for this substance.

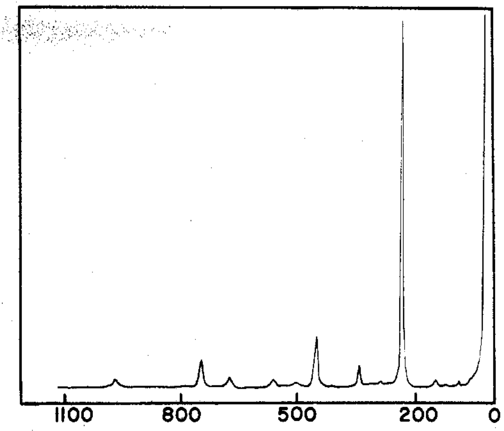

Figure 3. Solid-state Raman spectrum of the complex ion $[W_2OCl_{10}]^{4-}$ recorded using 5145-Å exciting radiation.

Figure 3 shows the Raman spectrum of this material. Several observations are immediately evident. First, the most prominent band is an intense spike appearing at 225 cm^{-1}. By analogy with the spectra observed for $[Ru_2OX_{10}]^{4-}$ and $[Os_2OCl_{10}]^{4-}$, we assign this as the symmetric W–O–W stretching frequency ν_1. This assignment is sustained by the solution depolarization ratio, $\rho = 0.31$, observed for this band in 12 *N* HCl using near-resonance 5145-Å exciting radiation. Second, two weaker bands appear at 338 and 282 cm^{-1}. The position of these bands suggests that they are metal–chlorine stretching modes. Again by analogy with the spectra of $[Ru_2OX_{10}]^{4-}$ and $[Os_2OCl_{10}]^{4-}$ we assign these bands as the radial chlorine–tungsten and terminal chlorine–tungsten stretching frequencies, $\nu_3(W–Cl_r)$ and $\nu_2(W–Cl_t)$, respectively. The remaining bands are tentatively assigned as follows: 450 ($2\nu_1$), 509 ($\nu_1 + \nu_2$), 562 ($\nu_1 + \nu_3$), 673 ($3\nu_1$), 898 cm^{-1} ($4\nu_1$).

The low value observed for the symmetric W–O–W stretching frequency suggests that the μ-oxo-decachloroditungstate ion contains a *linear* W–O–W geometry. This conclusion, combined with the other close similarities between Raman and infrared spectra of $[Ru_2OCl_{10}]^{4-}$ and $[Os_2OCl_{10}]^{4-}$ and those of $[W_2OCl_{10}]^{4-}$, implies that the μ-oxo-decachloroditungstate ion has the general structure shown in Figure 1.

$[Cr_2O(NH_3)_{10}]^{4+}$. Although the complex $[Cr_2O(NH_3)_{10}]Cl_4{\cdot}H_2O$ has been shown by single-crystal x-ray diffraction studies[22] to contain the linear μ-oxo-bridged ion $[Cr_2O(NH_3)_{10}]^{4+}$, we were prevented from obtaining the Raman spectrum of this substance because of its extreme photosensitivity.

Bent μ-Oxo-Bridged Complexes. Comparatively few bent μ-oxo-decahalo ions are known and none whose structure has been definitely established. Feltz[23] has reported the synthesis of a compound cited as tetrakis(tetraethylammonium) μ-oxo-decachlorodizirconium(IV), $[(C_2H_5)_4N]_4[Zr_2OCl_{10}]$, which was assigned a bent μ-oxo-bridged geometry based on vibrational studies. Repeated attempts to prepare this complex by the procedure described by Feltz produced in each instance a compound whose analytical and spectral data indicate it to be $[(C_2H_5)_4N]_4[ZrCl_6]$ (see Experimental Section).

The dichromate and ditungstate ions, $Cr_2O_7^{2-}$ and $W_2O_{11}^{2-}$, represent the best structurally characterized examples of simple bent μ-oxo-bridged transition metal complexes. Single-crystal x-ray and electron diffraction studies have established local

Table II. Bridge Vibrational Modes of Some Linear and Bent Mono-μ-oxo-Bridged Transition Metal Complexes

Species	∠M-O-M, deg	ν_{as}, cm^{-1}	ν_s, cm^{-1}	$\nu_{as} - \nu_s$, cm^{-1}
$K_4Ru_2OCl_{10}$	180	888	259	629
$Cs_4Ru_2OBr_{10}$	*a*	*b*	243	
$Cs_4Os_2OCl_{10}$	180	852	225	627
$W_2OCl_{10}^{4-}$	*a*	*b*	225	
$Cr_2O_7^{2-}$ [c]	115	740	570	170
$K_2W_2O_{11}$ [d]	140	790	556	234

[a] Undetermined. [b] Not observed. [c] For a fuller discussion of the vibrational spectra of dichromates, see ref 26. [d] Taken from ref 4.

C_{2v} symmetry for both of these ions. The average Cr–O–Cr bond angle is ~115°[24] while the W–O–W bond angle in $W_2O_{11}^{2-}$ is ~140°.[25] In addition, the vibrational spectra of crystalline dichromate[26] and ditungstate[4] salts have been examined. Detailed analyses have led to the following assignments: ν_{as}(Cr–O–Cr) ~740 cm^{-1}, ν_s(Cr–O–Cr) ~570 cm^{-1}, ν_{as}(W–O–W) ~790 cm^{-1}, and ν_s(W–O–W) ~556 cm^{-1}. To the extent that these observations can be extended to bent μ-oxo-bridged transition metal complexes in general, they are consistent with the conclusions of earlier approximate normal-coordinate studies,[4] i.e., that the symmetric metal–oxygen–metal stretch in bent μ-oxo bridged complexes occurs at a significantly higher frequency than in linear μ-oxo-bridged complexes while the asymmetric metal–oxygen–metal stretching vibration in bent complexes occurs at a significantly lower frequency in bent μ-oxo-bridged complexes than in linear μ-oxo-bridged complexes.

Although not a transition metal complex, the pyrophosphate ion, $P_2O_7^{2-}$, merits brief discussion at this point. An x-ray crystallography study has revealed the P–O–P bond angle in MnP_2O_7 to be ~130°.[27] On the basis of an examination of the infrared spectra of several pyrophosphate salts, Steger and Kässner concluded ν_{as}(P–O–P) is ~980 cm^{-1} while ν_s(P–O–P) is ~730 cm^{-1}.[28] These values are noticeably higher than the corresponding frequencies observed for the bent μ-oxo-bridged complex ions $Cr_2O_7^{2-}$ and $W_2O_{11}^{2-}$. However, it should be noted that the value for ν(P=O) observed for $P_2O_7^{2-}$ also occurs at an appreciably higher frequency (~1150 cm^{-1}) than the value typically observed for the oxy–metal stretching vibration, ν(M=O), which for most transition metal–oxy compounds falls between 980 and 800 cm^{-1}.[2] It is possible that this difference may simply reflect the potential difference between the force constant for ν(P=O) and that for ν(M=O), but this is not discernible from the present data. It remains significant, however, that the difference between ν_{as}(P–O–P) and ν_s(P–O–P) ($\Delta\nu$ = 250 cm^{-1}) is typical of the values observed for both $Cr_2O_7^{2-}$ and $W_2O_{11}^{2-}$ (cf. Table II).

Discussion

The principal purpose of this study was to demonstrate the diagnostic utility of Raman spectroscopy as a means of investigating and characterizing complexes that contain a single metal–oxygen–metal structural unit. It is apparent from the results obtained that, in the absence of interfering effects (vide infra), the Raman spectra of such complexes frequently display a band in the low-frequency region assignable as the symmetric metal–oxygen–metal stretching mode. The low value observed for ν_s(M–O–M) in linear μ-oxo-bridged structures contrasts sharply with the significantly higher value observed for ν_s(M–O–M) in bent μ-oxo-bridged systems. An examination of Table II suggests that the magnitude of this difference, i.e., $\nu_{as} - \nu_s$, may provide a useful means of distinguishing between these two structural types. A comparison of these results with the purportedly equivalent data obtained from infrared studies[5] indicates that the latter are not, in general, reliable for such determinations.

This investigation has provided various additional insights into the structural nature of certain complexes. The isostructural relationship between $[W_2OCl_{10}]^{4-}$ and $[Ru_2OCl_{10}]^{4-}$ and $[Os_2OCl_{10}]^{4-}$ as well as the indicated differences between the terminal and radial chlorine–ruthenium bond distances in $[Ru_2OCl_{10}]^{4-}$ are two particular examples. In conclusion, it should be noted that the Raman spectra of the linear μ-oxo-bridged complexes reported here display distinct resonance-Raman character: relative band intensities show a marked dependence on the frequency of the exciting radiation as well as typically strong overtone and combination bands, the half-widths of which increase progressively with increasing vibrational quantum number.[29] The information obtained from a detailed examination of these effects can be useful in interpreting the electronic spectra of these complexes.[30] However, from a practical point of view, such effects can sometimes prove unwanted. Such is the case, for example, with the linear μ-oxo-bridged dimer of [*meso*-tetraphenylporphyrin]iron(III), $[(TPP)Fe]_2O$, the structure of which has been established by x-ray crystallography.[31] The Raman spectrum of this compound obtained with 5145-Å exciting radiation does not display any low-frequency bands (<350 cm^{-1}) which could be readily assigned as ν_s(Fe–O–Fe), presumably because of the significantly greater enhancement suffered by ligand-related modes. Presumably, this effect could be lessened by employing an exciting frequency that fell well outside the electronic envelope. Unfortunately, such instrumentation is not widespread. Therefore, the absence of a low-frequency band corresponding to ν_s(M–O–M) is not, of itself, a sufficient criterion to dispel the presence of a linear μ-oxo-bridged structure in those instances where moderate to strong interfering resonance-Raman effects are present.

Experimental Section

Materials. Osmium and ruthenium tetraoxides were purchased from Alfa Inorganics and used without further purification. Potassium and cesium chlorides and bromides (99% pure) were obtained from several commercial sources and used as received. Tin powder (325 mesh) was purchased from Research Organic/Inorganic.

Spectra and Analyses. Raman spectra were recorded on a Cary Model 82 laser Raman spectrometer equipped with a rotating sample cell similar to that described elsewhere.[32] 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. Excitation was provided by Coherent Radiation Laboratory Model 52 argon and krypton ion lasers. Reported frequencies are precise to ±1 cm^{-1}. Infrared spectra were recorded on a Perkin-Elmer Model 225 spectrophotometer employing either KBr disks or Nujol mulls supported on polyethylene plates. Frequencies are precise to ±1 cm^{-1}. Elemental analyses were determined by Galbraith Laboratories, Knoxville, Tenn.

$[Cr_2O(NH_3)_{10}]Cl_4 \cdot H_2O$ was prepared by a literature procedure.[22]

Tetrapotassium μ-Oxo-decachlorodiruthenium(IV). The following procedure is an adaptation of the method described by Woodhead and Fletcher.[33] Into a 250-ml flask equipped with a Teflon-coated stirrer bar was placed ruthenium tetraoxide (1.0 g, 6.0 mmol) and 100 ml of 3 *N* HCl. The flask was stoppered and the solution stirred for 12 hr before adding an aqueous solution of potassium chloride (2.5 g in 10 ml). The total volume of the resulting solution was reduced to ~30 ml on a steam bath and then cooled in an ice bath. The resulting dark brown crystalline precipitate (1.5 g) was collected in a sintered-glass funnel by suction filtration, washed with two 15-ml portions of absolute ethanol followed by two 15-ml portions of absolute ether. Recrystallization was accomplished by dissolving the initial product in 50 ml of 6 *N* hydrochloric acid and concentrating to a volume of 25 ml on a steam bath. The isolated yield was 1.14 g (52%). Anal. Calcd for $K_4Ru_2OCl_{10}$: Cl, 48.69. Found: Cl, 48.69.

Tetracesium μ-Oxo-decachlorodiruthenium(IV), $Cs_4Ru_2OCl_{10}$, was obtained in quantitative yield by treating a solution of $K_4Ru_2OCl_{10}$ (0.50 g) in 6 *N* HCl (20 ml) with a solution of cesium chloride (1.0 g) in 6 *N* HCl (10 ml). Anal. Calcd for $Cs_4Ru_2OCl_{10}$: Cl, 32.10. Found: Cl, 32.67.

Tetracesium μ-Oxo-decabromodiruthenium(IV), $Cs_4Ru_2OBr_{10}$. Into a 250-ml flask equipped with a Teflon-coated stirring bar was placed ruthenium tetraoxide (1.00 g, 6.00 mmol) and 100 ml of 3 *N* hydrobromic acid. The flask was stoppered and the mixture stirred at room temperature for 24 hr. The resulting dark red solution was subsequently reduced to a volume of ~30 ml on a steam bath and allowed to cool to room temperature before treating with a solution of cesium bromide (2.0 g) in 6 *N* HBr (10 ml). The subsequent solution was boiled for 60 sec and then allowed to cool gradually. The dark violet, crystalline precipitate that formed was collected in a fritted glass funnel by suction filtration and rinsed with two 15-ml portions of absolute ethanol followed by two 15-ml portions of absolute ether. The isolated yield was 99%. Anal. Calcd for $Cs_4Ru_2OBr_{10}$: Br, 51.59. Found: Br, 51.68.

Tetrapotassium μ-Oxo-decabromodiruthenium(IV), $K_4Ru_2OBr_{10}$, was prepared by a procedure analogous to that described above for the preparation of $Cs_4Ru_2OBr_{10}$. The solution resulting from the reaction of 50 ml of 3 *M* HBr with 0.50 g (3.0 mmol) of ruthenium tetraoxide was concentrated to ~15 ml on a steam bath and treated with a solution of potassium bromide (1.5 g) in 6 *M* HBr (5 ml). This mixture was boiled for 60 sec and then allowed to cool gradually to room temperature before chilling at −15°. The crystalline product (0.46 g) was isolated by suction filtration in 13% yield. Anal. Calcd for $K_4Ru_2OBr_{10}$: Br, 68.09. Found: Br, 68.03.

Tetrapotassium μ-Oxo-decachlorodiosmium(IV), $K_4[Os_2OCl_{10}]$, was prepared by a modification of the procedure described by Dwyer and Hogarth[34] for the preparation of tetraammonium μ-oxo-decachlorodiosmium(IV) $[NH_4]_4[Os_2OCl_{10}]$. Into a 25-ml flask was placed osmium tetraoxide (0.50 g, 2.0 mmol) and a solution of ferrous sulfate (2.5 g), potassium chloride (0.60 g), 1.5 ml of 12 *N* HCl, 2 ml of 10 *N* H_2SO_4, and 8 ml of distilled water. The flask was tightly stoppered and heated gently on a steam bath for 2 hr. The resulting mixture was allowed to stand overnight and suction filtered, and the filtrate was treated with 5 ml of a saturated solution of potassium chloride in 6 *M* HCl. After standing for 30 min, the flask was chilled at −15° for 24 hr. The dark red-brown crystals that deposited were collected by suction filtration and rinsed with two 15-ml portions of absolute ethanol followed by two 15-ml portions of absolute ether and dried in vacuo. The isolated yield was 0.047 g (5.27%). Anal. Calcd for $K_4Os_2OCl_{10}$: Cl, 39.07. Found: Cl, 38.78.

Tetracesium μ-Oxo-decachlorodiosmium(IV), $Cs_4[Os_2OCl_{10}]$. This material was prepared by a procedure similar to that described above for the preparation of $K_4[Os_2OCl_{10}]$. Osmium tetraoxide (0.50 g, 2.0 mmol) was added to a solution consisting of ferrous sulfate (2.5 g), cesium chloride (0.30 g), 1.5 ml of 12 *M* HCl, 2 ml of 10 *N* H_2SO_4, and 8 ml of distilled water contained in a 25-ml flask. The flask was stoppered, heated for 2 hr on a steam bath, and then allowed to cool to room temperature and stand overnight. Following suction filtration the filtrate was treated with a solution of cesium chloride (4.0 g) in 20 ml of 6 *M* HCl. The resulting solution was heated for several minutes on a steam bath, allowed to cool gradually to room temperature, and then chilled at −15° for 24 hr. The crystals that deposited (0.177 g) were collected by suction filtration. A second crop was obtained by evaporating the mother liquor to near dryness and adding distilled water dropwise to dissolve the extraneous iron and cesium salts. The combined products (0.183 g, 14%) were rinsed as before and dried in vacuo. Anal. Calcd for $Cs_4Os_2OCl_{10}$: Cl, 27.44. Found: Cl, 27.43.

$[W_2OCl_{10}]^{4-}$. Hydrochloric acid (12 *M*, 75 ml) was placed in a three-necked, 250-ml flask equipped with a Teflon-coated stirrer bar. The flask was chilled to −20° and the contents saturated with gaseous hydrogen chloride. To this solution was added a suspension of potassium tungstate, prepared by the addition of tungstic acid (2.8 g, 0.011 mol) and potassium carbonate (3.0 g, 0.022 mol) to 20 ml of distilled water. The addition was made slowly with a continuous flow of hydrogen chloride gas through the reaction mixture. During the course of the addition (ca. 75 min) the temperature was not allowed to rise above −15°C. Following the completion of addition, concentrated hydrochloric acid (25 ml) was added, the cold bath was removed, and the solution was allowed to warm to room temperature while still maintaining a flow of hydrogen chloride gas. The resulting solution was filtered and returned to the reaction vessel. Once again hydrogen chloride gas was introduced into the solution while the vessel was cooled to −20°. Tin powder (9 g; 325 mesh) was added slowly over a period of 60 min, such that the temperature did not rise above −15°C. The solution turned deep blue after the initial addition of tin, then to a deep violet, and finally to dark red. At this point a crystalline material was observed in the flask. The solution was suction filtered and the dark red crystalline material washed with two 15-ml portions of ice-cold anhydrous ethanol then two 15-ml portions of anhydrous diethyl ether. The resulting solid weighed 3.75 g. Analytical data varied somewhat from preparation to preparation. Anal. Calcd for $K_4W_2OCl_{10}$: K, 17.48; W, 41.10; Cl, 39.63. Found: K, 17.70; W, 35.02; Cl, 42.26; Sn, 5–10.

Attempted Preparation of $[(C_2H_5)_4N]_4[Zr_2OCl_{10}]$. The following procedure is reported to yield the tetraethylammonium salt of the bent μ-oxo-bridged decachloro ion $[Zr_2OCl_{10}]^{4-}$.[23] Under an atmosphere of dry, prepurified nitrogen, zirconium tetrachloride (41.2 g, 0.177 mol) was placed in a flame-dried 500-ml, three-necked flask equipped with a nitrogen inlet and a dropping funnel. The unstoppered arms were capped with rubber septums. Acetonitrile (300 ml, freshly distilled from P_2O_5 under a nitrogen atmosphere) was added by cannula. A solution of freshly distilled acetonitrile (50 ml) containing 1.6 ml of water was added dropwise to this solution over a 2-hr period. The reaction mixture was purged with dry nitrogen during and for 2 hr following the completion of addition to remove the hydrogen chloride gas which formed. A distilling head was attached and the solvent removed by distillation under nitrogen. The residue was then heated at 100° (0.5 mmHg) for 2 hr. A portion (7.39 g) of the resulting product, reported[23b] to be $Zr_2OCl_6 \cdot 4CH_3CN$, was transferred under an atmosphere of dry nitrogen to a 100-ml flame-dried flask which was then stoppered with a rubber septum. Acetonitrile (freshly distilled from P_2O_5) was added by syringe and the solution heated until the solid dissolved. The resulting solution was then cooled to −20° and an ice-cold suspension of tetraethylammonium chloride (12.5 g) in dry acetonitrile (40 ml) was quickly added. The white precipitate which formed immediately was collected by suction filtration, washed with cold acetonitrile, and dried in vacuo. Anal. Calcd for $[(C_2H_5)_4N]_4Zr_2OCl_{10}$: C, 35.79; H, 7.46; Cl, 33.04; N, 5.22. Found: C, 33.91; H, 7.25; Cl, 37.53; N, 5.00.

Repeated attempts yielded similar results and equivalent analytical data which are consistent with the formulation of this material as $[(C_2H_5)_4N]_2[ZrCl_6]$. Anal. Calcd for $[(C_2H_5)_4N]_2[ZrCl_6]$: C, 34.05; H, 7.09; Cl, 37.72; N, 4.97. Moreover, the Raman spectrum of this substance, as well as that reported by Feltz[23a] for the purported compound $[(C_2H_5)_4N]_4[Zr_2OCl_{10}]$, are equivalent to that observed for an authentic sample of $[(C_2H_5)_4N]_2[ZrCl_6]$.

Tetraethylammonium Hexachlorozirconate(IV), $[(C_2H_5)_4N]_2[ZrCl_6]$. Anhydrous tetraethylammonium chloride (16 g, 0.1 mol) was placed in a 100-ml flame-dried flask which was then stoppered with a rubber septum and flushed with dry nitrogen. Zirconium tetrachloride (Alfa Inorganics; 11.7 g, 50 mmol) was placed in a second 100-ml flame-dried flask which was quickly stoppered with a rubber septum and flushed with dry nitrogen. Anhydrous ethanol (40 ml) was added to each flask and the contents swirled to promote dissolution. Both mixtures were then cooled to 0° and saturated with dry gaseous hydrogen chloride. Admixture of these two solutions resulted in the immediate precipitation of a white, microcrystalline material which was collected by suction filtration and washed with two 15-ml portions of ice-cold anhydrous ethanol, followed by two 15-ml portions of anhydrous ether, and was finally dried in vacuo. The yield was virtually quantitative. Anal. Found: C, 33.88; H, 7.45; N, 477; Cl, 37.50. Raman spectrum (solid): 1459 (m), 1448 (w–m), 1305 (w), 1122 (w), 1077 (m), 1036 (vw), 898 (w–m), 794 (vw), 665 (m), 472 (vw), 393 (w–m), 327 (s), 149 (vs), 61 (m–s) cm^{-1}.

Registry No. $K_4[Ru_2OCl_{10}]$, 16986-07-5; $Cs_4[Ru_2OCl_{10}]$, 57304-86-6; $Cs_4[Ru_2OBr_{10}]$, 57304-87-7; $K_4[Ru_2OBr_{10}]$, 16925-36-3; $K_4[Os_2OCl_{10}]$, 57304-88-8; $Cs_4[Os_2OCl_{10}]$, 57304-89-9; $K_4[W_2OCl_{10}]$, 19644-53-2; $[(C_2H_5)_4N]_2[ZrCl_6]$, 21439-27-0; $[(C_2H_5)_4N]_4[Zr_2OCl_{10}]$, 19189-75-4.

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viz., that involving a simultaneous in-phase, out-of-plane "umbrella" vibration involving all and only the radial halogens. As suggested by studies of octahedral anions $[MCl_6]^{n-}$, such modes invariably fall *below* (usually significantly below) 200 cm^{-1}.
(10) The theory of resonance Raman scattering predicts that the resonance involving a single electronic transition enhances a single element of the Raman scattering tensor,[11] and if that element dominates the intensity, then the depolarization ratio, ρ_1, for a totally symmetric vibration (A_g) approaches 1/3 at that resonance.[12]
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Mechanistic Studies on the Vanadium(II) and Vanadium(III) Reductions of Iodate and Bromate

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The kinetics of the vanadium(III) reduction of iodate have been investigated over a wide range of conditions, $\mu = 1.0$ *M* ($LiClO_4$). Rate constants, $[H^+] > 0.25$ *M*, are dependent on the ratio of reactants *R* ($=[V(III)]_i/[I(V)]_i$) implying that disproportionation of an intermediate oxidation state, probably I(III), is effective at low V(III). The dependence of rate constants on $[H^+]$ indicates that the reaction proceeds by paths $V^{3+} + IO_3^-$ and/or $VOH^{2+} + HIO_3$, and the temperature dependence has been studied, 3–35°C. The V(II) reduction of iodate proceeds in 1-equiv steps. Rate constants obtained from consecutive reaction treatment, $[H^+] = 0.5$–1.0 *M*, suggest that the pathway $V^{2+} + HIO_3$ ($k \geq 360$ M^{-1} sec^{-1} at 25°) is dominant. Brief studies of the V(II) and V(III) reductions of bromate have also been made. With V(II) small (0.07%) contributions from a 2-equiv process giving VO^{2+}, and hence the highly absorbing V^{III}_2 species as an intermediate, were detected.

Iodate and bromate function as 2-equiv oxidants in the reaction with hydrazine and sulfite.[1] Although many studies have been made of reactions of chlorate and bromate with metal complexes,[2–12] the reactions of iodate have with one exception[13] been neglected. Bromate is known to undergo a 2-equiv change in the oxidation of the mercury(I) dimer,[14] but 1-equiv changes are effective in other cases. We consider here the iodate and bromate oxidations of V(II) and V(III), both of which might be regarded as potential 2-equiv reductants. The single-stage change $V^{2+} \rightarrow VO^{2+}$ has been observed previously[15–17] and is clearly a possibility. The single-stage $V^{3+} \rightarrow VO_2^+$ change has not been detected, however,[18,19] and is more difficult to bring about because of the extensive change in degree of hydrolysis. The studies with iodate which we report are more extensive than those with bromate, which amount to little more than semiquantitative observations.

Experimental Section

Solutions of vanadium(II), vanadium(III), and vanadium(IV) perchlorates, lithium perchlorate, and perchloric acid were prepared as described previously.[15] Iodic acid (BDH Analar) and potassium bromate (Fisons Analytical Reagent) were used without further purification. A nitrogen gas stream was used to deoxygenate all solutions. Atlas nylon syringes, stainless steel needles, and rubber serum caps were used to maintain air-free conditions. Ionic strengths were adjusted to $\mu = 1.00$ *M* ($LiClO_4$). Unless otherwise stated reactions were followed spectrophotometrically using a Durrum-Gibson stopped-flow spectrophotometer.

Results

The Reaction of V(III) with Iodate. With a large excess of V(III) products VO^{2+}, λ_{max} 760 nm (ϵ 17.2 M^{-1} cm^{-1}), and I_2, λ_{max} 460 nm (ϵ 746 M^{-1} cm^{-1}),[20] are obtained in the first stage. Stopped-flow measurements indicate that 0.46 ± 0.05 mol of I_2 and 5.02 ± 0.4 mol of VO^{2+} are formed for each mole of iodate present initially. On completion of a second stage no I_2 remains and 6.0 ± 0.1 mol of VO^{2+} is produced for each mole of iodate. The two stages of the reaction can thus be summarized as in (1) and (2). The second stage has

$$5V(III) + I(V) + 2H_2O \rightarrow {}^1/_2I_2 + 5VO^{2+} + 4H^+ \tag{1}$$

$$V(III) + {}^1/_2I_2 + H_2O \rightarrow I^- + VO^{2+} + 2H^+ \tag{2}$$

been studied independently by Ramsay and Heldman[21] and from their data the half-life at 25°, $[H^+] = 0.5$ *M*, [V(III)]