

THE NATURE AND SPECTROSCOPIC CHARACTER OF THE METAL-OXYGEN BONDING OF SOME HEAVY METALS

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The infra-red spectra of compounds containing metal-oxygen bonds, *viz.*, mono-oxy- and hydroxy-compounds of rhenium, ruthenium and osmium of the general formulae $MO_nL_{6-n}^{x-}$ ($n=1$ with $M = \text{Re, Os}$; $n = 2$ with $M = \text{Re, Ru, Os}$ and $n = 3$ with $M = \text{Re, Os}$), $[\text{MO}(\text{OH})L_4]^y$, ($M = \text{Re}$), $[\text{M}(\text{OH})_2L_4]^{z-}$ ($M = \text{Re, Ru, Os}$) and MO_4^k ($k = 0, -1, -2$ and $M = \text{Re, Ru, Os}$) and those of binuclear compounds containing the oxygen bridge *MOM* were examined. On the basis of group theory the normal modes and correlation tables for all possible structures of these compounds were compiled, and the particular bands were assigned to the corresponding functional groups. Approximate expressions for calculation of force constants in the metal-oxygen bonds existing in the oxycompounds of rhenium, ruthenium and osmium were derived. A comprehensive discussion of the results obtained is presented.

Introduction

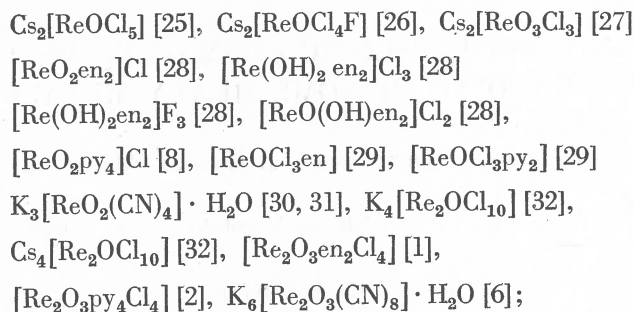
The oxygen atom forms strong bonds with metal atoms. These bonds result both from σ and π interactions. The metal oxycations MO_n^{x+} and oxyanions MO_m^{y-} are stable in solid and liquid phases and in solutions. Owing to its electrodonor properties, the oxygen atom can also form a connecting bridge between the metal atoms to yield stable *MOM* groups. These oxygen bridges make possible the occurrence of a peculiar kind of superexchange between the metal atoms, which may result in complete spin quenching of the metal atoms. This extreme case was called "oxygen bonding". Vibrational spectroscopy is a good tool for discerning the character of the chemical bonds, *i.e.* the interactions between the atoms of oxygen and metal. This method permits to determine the molecular structure and type of interactions, and to establish the extent of the π character in the bonding as well. The present studies were made on heavy transition metals — rhenium, ruthenium and osmium — where the tendency to form π -bondings is particularly evident.

Earlier papers on the vibrational spectroscopy of rhenium [1–15] and osmium [16–18] oxy-compounds dealt only with the limited spectral region ($650\text{--}1000\text{ cm}^{-1}$) and did not contain any theoretical band assignment. From among the ruthenium oxycomplexes, only

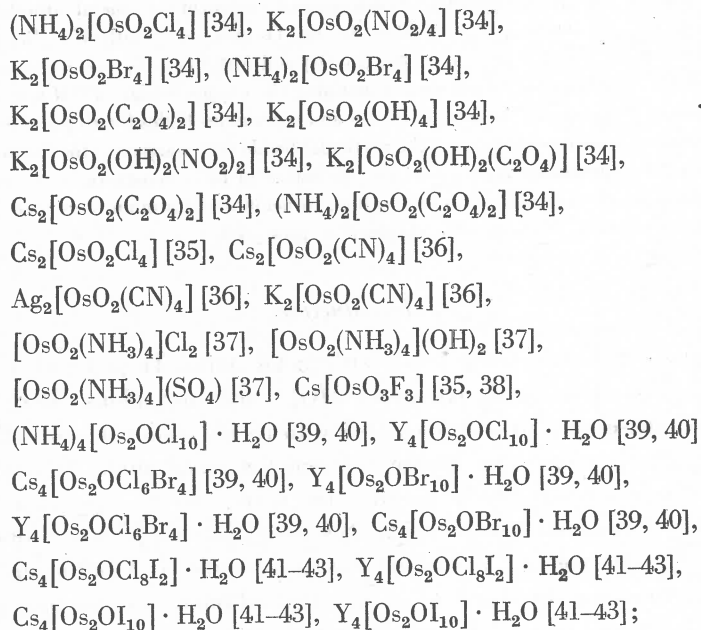
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the tetrahedral compounds were subject to spectroscopic studies [19–24]. In our paper, we present the result of infra-red studies over a 200–4000 cm^{-1} range (Perkin-Elmer Grating Spectrophotometer, Model 621) on the following oxy- and hydroxy-compounds:

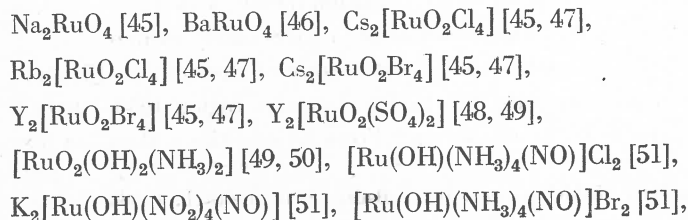
— for rhenium: ReO_2 , KReO_4 , CsReO_4 , $\text{K}_2[\text{ReOCl}_5]$ [25]

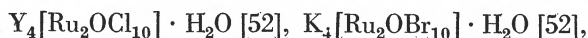
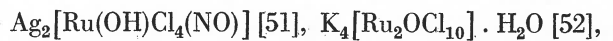


— for osmium: OsO_4 (gas and solid), OsOF_5 [33], $\text{K}_2[\text{OsO}_2\text{Cl}_4]$ [34]



— for ruthenium: RuO_4 (gas and solid), KRuO_4 , NaRuO_4 [44],





where $\text{Y} = [\text{As}(\text{phen})_4]$.

For comparison and elimination of metal-halogen bands, the spectra of the following simple complexes were procured:

— for rhenium: K_2ReCl_6 [53], Cs_2ReCl_6 [53], K_2ReF_6 [53],

Cs_2ReF_6 [53], $\text{Cs}[\text{Re}(\text{CN})_6] \cdot \text{H}_2\text{O}$ [54],

$\text{Y}[\text{Re}(\text{CN})_6] \cdot \text{H}_2\text{O}$ [54];

— for ruthenium: K_2RuCl_6 [45], K_2RuBr_6 [45, 50];

— for osmium: K_2OsCl_6 [39], K_2OsBr_6 [39], K_2OsI_6 [39], K_2OsF_6 [55].

The above complexes were obtained by the methods described in the papers referred to at each particular compound. The compounds examined by us are divided into two groups, one with pseudotetrahedral symmetry and the other with pseudooctahedral symmetry.

Compounds with pseudotetrahedral symmetry

Perrhenates were studied by several authors [56–61]. Griffith [56], Kriegsmann [57, 61] and Petrov [59] have established T_d symmetry of the anion on the basis of IR and Ra spectra in aqueous solutions. These studies, as well as those made by Baran [62] and Busey [60] in the solid state, were used by Müller and Krebs [24] for their calculations of force constants in the ReO_4 anion. In our opinion, the T_d symmetry is not a good approximation of the actual structure of this anion in the solid state. On the basis of group theory we have compiled a correlation table of symmetry groups for a distorted tetrahedron (Table I).

TABLE I

Correlation table of the symmetry groups for a distorted tetrahedron

	T_d	C_{3v}	C_{2v}	C_s	C_2	C_3	S_4
ν_1	$A_1(R)$	$A_1(I, R)$	$A_1(I, R)$	$A'(I, R)$	$A(I, R)$	$A(I, R)$	$A(R)$
ν_2	$E(R)$	$E(I, R)$	$A_1(I, R) +$ $+ A_2(R)$	$A''(I, R)$	$2A(I, R)$	$E(I, R)$	$A(R) +$ $+ B(I, R)$
ν_3	$F_2(I, R)$	$A_1(I, R) +$ $+ E(I, R)$	$A_1(I, R) +$ $+ B_1(I, R) +$ $+ B_2(I, R)$	$2A'(I, R) +$ $+ A''(I, R)$	$A(I, R) +$ $+ B(I, R) +$ $+ B(I, R)$	$A(I, R) +$ $+ E(I, R)$	$B(I, R) +$ $+ E(I, R)$
ν_4	$F_2(I, R)$	$A_1(I, R) +$ $+ E(I, R)$	$A_1(I, R) +$ $+ B_1(I, R) +$ $+ B_2(I, R)$	$2A'(I, R) +$ $+ A''(I, R)$	$A(I, R) +$ $+ B(I, R) +$ $+ B(I, R)$	$A(I, R) +$ $+ E(I, R)$	$B(I, R) +$ $+ E(I, R)$

The spectra of perrhenates and the oxide ReO_2 are given together with their assignments in Table II.

According to the correlation table, KReO_4 has S_4 symmetry. This is shown by the absence of the $\nu(\text{Re}=\text{O})$ at 965 cm^{-1} and the presence of doublets $\delta(\text{OReO})$ and $\nu(\text{ReO}_4)$. In the case of CsReO_4 the presence of the $\nu(\text{Re}=\text{O})$ band and triplets of the above bands are characteristic of the C_s symmetry.

A definite symmetry may also be assigned to the oxide ReO_2 . The arrangement and intensities of its bands are evidence of pseudotetrahedral structure. The absence of the $\nu(\text{Re}=\text{O})$ band at about 970 cm^{-1} and the splitting of other bands correspond to the S_4

TABLE II

Cs ReO_4		K ReO_4	ReO_2	Symmetry S_4
Spectrum	Symmetry C_s	Spectrum	Spectrum	
		—	245 <i>w</i>	} $\delta(\text{O}^*\text{ReO}) B$ $\delta(\text{O}^*\text{ReO}^*) E$
		—	278 <i>m</i>	
318 <i>w, sh</i>	$\delta(\text{OReO}) A''$	305 <i>vs</i>	305 <i>vs</i>	$\delta_{as}(\text{OReO}) B$
328 <i>vs</i>	$\delta(\text{OReO}) A'$	314 <i>vs</i>	315 <i>s</i>	$\delta_s(\text{OReO}) E$
335 <i>s</i>	$\delta(\text{OReO}) A'$			
345 <i>m</i>	$\delta(\text{ReO}_4) A''$	365 <i>s</i>	363 <i>m</i>	$\delta(\text{ReO}_4) B$
		—	466 <i>w, vvb</i>	$\nu_s(\text{ReORe})$ or $\nu(\text{ReO})$
		—	736 <i>w, vvb</i>	$\nu_{as}(\text{ReORe})$
901 <i>vs</i>	$\nu(\text{ReO}_4) A''$			
915 <i>vs</i>	$\nu(\text{ReO}_4) A'$	913 <i>vs</i>	911 <i>vs, b</i>	$\nu_{as}(\text{ReO}_4) E$
931 <i>s, sh</i>	$\nu(\text{ReO}_4) A'$	930 <i>vs, sh</i>	939 <i>vs, sh</i>	$\nu_s(\text{ReO}_4) B$
967 <i>w</i>	$\nu(\text{Re}=\text{O}) A'$	965		$\nu(\text{Re}=\text{O}) A$ (calc. from comb. band).
1866 <i>w</i>	{ 967+901 2×931	1859 <i>m</i>	1858 <i>m</i>	2×930
1880 <i>w</i>	967+915	1870 <i>w, sh</i>		965+913
1905 <i>w</i>	967+931	1903 <i>w</i>		965+930

symmetry. The two weak bands appearing between 200 and 300 cm^{-1} result from the deformation vibrations $\delta(\text{O}^*\text{ReO})$ and $\delta(\text{O}^*\text{ReO}^*)$, where the $\text{Re}-\text{O}^*$ bonding is somewhat longer with respect to $\text{Re}-\text{O}$. Two new bands, very diffuse and weak, are also observed over the $450\text{--}750\text{ cm}^{-1}$ region. Such arrangement of bands (three bands above 400 cm^{-1}) is characteristic of most oxides. The band at 466 cm^{-1} results most probably from the $\nu_s(\text{ReORe})$ or $\nu(\text{Re}-\text{O})$ vibrations, since the ReORe system seems to be angular in this case. The absorption at 736 cm^{-1} was assigned to the asymmetric stretching vibrations of the angular ReORe group existing in the space lattice.

The infra-red spectra of the respective osmium and ruthenium compounds are shown in Table III and IV.

The infra-red spectra of osmium [20, 23, 63, 64] and ruthenium [19–24] oxy-compounds of a general formula MO_4 are extensively discussed in the literature. The spectra of these

TABLE III

OsO ₄ gas	OsO ₄ solid	RuO ₄ gas	RuO ₄ solid	T _d
970	962	873	—	$\nu_1(A_1)^*$
960 <i>vs, b</i>	945 <i>s, sh</i> 956 <i>s</i>	920 <i>vs, b</i>	{ 906 <i>s, sh</i> 924 <i>s</i>	$\nu_3(F_2)$
329 <i>s, b</i>	321 <i>w, sh</i> 331 <i>s</i>	329 <i>s, b</i>	{ 329 <i>s</i> 336 <i>m, sh</i>	$\nu_4(F_2)$
1930 <i>w</i>	—	1793 <i>m</i>	—	$\nu_1 + \nu_3$
1920 <i>w</i>	1918 <i>vw</i>	1828 <i>w</i>	—	$2\nu_3$

* $\nu_1(A_1)$ calculated from combination bands.

compounds in the solid and gas state (Table III), when compared with the correlation table (Table I), enable to establish T_d symmetry in these oxides. This is shown by the absence of the $\nu_1(A_1)$ and $\nu_2(E)$ bands, which are forbidden in the infrared. The values of $\nu_1(A_1)$ given in the table have been calculated from the combination bands. A slight splitting of the $\nu_3(F_2)$ and $\nu_4(F_2)$ bands in the solid state results from the crystal field effect. The lowering

TABLE IV

Na RuO ₄	K RuO ₄	Symmetry S ₄	K ₂ RuO ₄	Ba RuO ₄	C _s
283 <i>s</i>	279 <i>s, sh</i>	$\delta_{as}(ORuO) B$	301 <i>w, sh</i>	294 <i>w, sh</i>	$\delta(O RuO) A''$
287 <i>s</i>	285 <i>s</i>	$\delta_s(O RuO) E$	320 <i>vs</i>	321 <i>vs, b</i>	$\delta(O RuO) A'$
334 <i>w</i>	330 <i>m</i>	$\delta(RuO_4) B$	328 <i>s, sh</i>	334 <i>s, sh</i>	$\delta(O RuO) A'$
			334 <i>m</i>	338 <i>m</i>	$\delta(RuO_4) A''$
828 <i>m</i>	825 <i>m</i>	$\nu_{as}(RuO_4) E$	802 <i>m, sh</i>	805 <i>s, sh</i>	$\nu(RuO_4) A''$
			807 <i>vs</i>	813 <i>vs</i>	$\nu(RuO_4) A'$
851 <i>s</i>	849 <i>s</i>	$\nu_s(RuO_4) B$	835 <i>s, sh</i>	832 <i>s, sh</i>	$\nu(RuO_4) A'$
—	864	$\nu(Ru=O)^* A$	859 <i>m</i>	856 <i>m</i>	$\nu(Ru=O) A'$
—	1652 <i>w</i>	$2 \times \nu_{as}$	1671 <i>w</i>	1669 <i>w</i>	$\nu(Ru=O) + \nu(RuO_4)$
—	1713 <i>vw</i>	$\nu(Ru=O) + \nu_s(RuO_4)$	1698 <i>w</i>	1680 <i>w</i>	$\nu(Ru=O) + \nu(RuO_4)$

* $\nu(Ru=O)A$ calculated from combination bands.

symmetry in solid state may be observed in the vibrational spectra of the ruthenium oxyanions (Table IV). According to the correlation table, the ruthenates have S₄ symmetry, as shown by the occurrence of the $\delta(O RuO)$ and $\nu(RuO_4)$ doublets and the absence of the $\nu(Ru=O)$ band. The RuO₄⁻ oxyanions have still lower symmetry in the solid state, since the band arrangement in the spectra with a triplet band structure is characteristic of the C_s symmetry.

Complex compounds with pseudo-octahedral symmetry

A theoretical treatment of normal vibrations in pseudo-octahedral oxy-compounds of a general formula $[MO_nL_{6-n}]^x$ is presented in Table V.

This table enables an accurate assessment of the complex symmetry to be made, since the isomeric structure of a compound may be determined from the number of the $\nu(MO)$ and $\nu(ML)$ bands. The particular classes of compounds will be discussed in detail.

TABLE V

Normal vibrations of the $MO_nL_{6-n}^{x-}$ systems.

Type of compound	Isomer	Symmetry	$\nu(MO)$		$\nu(ML)$		Irreducible representation of the group
			Representation	Numb. of IR bands	Representation	Numb. of IR bands	
MOL_5	—	C_{4v}	A_1	1	$2A_1+B_1+E$	3	$4A_1+2B_1+B_2+4E$
MO_2L_4	trans	D_{4h}	$A_{1g}+A_{2u}$	1	$A_{1g}+B_{1g}+E_u$	1	$2A_{1g}+B_{1g}+B_{2g}+E_g+2A_{2u}+3E_u$
	cis	C_{2v}	A_1+B_1	2	$2A_1+B_1+B_2$	4	$6A_1+2A_2+4B_1+3B_2$
MO_3L_3	trans	C_{2v}	$2A_1+B_1$	3	$2A_1+B_2$	3	$6A_1+A_2+4B_1+4B_2$
	cis	C_{3v}	A_1+E	2	A_1+E	2	$4A_1+A_2+5E$ (degener.)
MOL_3X_2	trans	C_{2v}	A_1	1	$2A_1+B_1$	3	$4A_1+B_1+B_2$
	cis	C_s	A'	1	$2A'+A''$	3	$4A'+2A''$

A. The MOL_5 type compounds

The molecule of a general formula XY_5Z and C_{4v} symmetry has been theoretically discussed by Griffiths [65], Cross [66], Smith [67] *et al.* on the basis of the spectra of SF_5Cl and IOF_5 . The notation employed by these authors is used aside our own in considerations of the bond vibrations in these compounds. For comparison, the infra-red spectra of the ML_6^- type anions (Table VI) were found in order to obtain the data on the metal-halogen bond frequency which is necessary for further discussion.

TABLE VI

Cs_2ReCl_6	K_2ReCl_6	K_2ReF_6	Cs_2ReF_6	K_2OsCl_6	K_2OsBr_6	K_2OsF_6	K_2OsI_6	K_2RuCl_6	K_2RuBr_6	Assignment
309 vs	317 vs	540 vs	528 vs	325 vs	224 vs	548 vs	n. o.	328 vs	250 s	$\nu_3(F_{1u})\delta(LML)$
n. o.	n. o.	235 vs	238 vs	n. o.	n. o.	$\left. \begin{matrix} 262 s \\ 246 sh \end{matrix} \right\}$	n. o.	n. o.	n. o.	$\nu_4(F_{1u})-\nu(ML)$

The abbreviation "n.o." denotes the frequencies which we could not observe because they lie below 200 cm^{-1} .

Table VII contains the infra-red spectra of $ReOCl_5^-$, $ReOCl_4F^-$ and $OsOF_5^-$. L' denotes the ligand atom (Cl, F) in trans position with respect to the oxygen. The broad

TABLE VII

Species	Activity	Assignment*	Denotations**	$K_2[ReOCl_5]$.aq	$Cs_2[ReOCl_5]$.aq	$Cs_2[ReOCl_4F]$	$OsOF_5$ gas.
—	—	$\nu(OH)$		3340 <i>w, b</i>	3540 <i>m, b</i>	—	—
—	—	$\delta(HOH)$		1635 <i>m, b</i>	1605 <i>s, b</i>	—	—
A_1	IR, Ra	$\nu(M=O)$	$\nu_1(M=O)$ axial stretch	993, 988 <i>vs</i>	955 <i>vs</i>	973 <i>vs</i>	960 <i>vs</i>
		$\nu_s(ML_4)$	$\nu_2(ML_4)$ sym. square stretch	316 <i>vs, b</i>	310 <i>vs, b</i>	305 <i>vs, b</i>	712 <i>vs</i>
		$\gamma(ML_4)$	$\nu_3(ML_4)$ out of plane deform.	275 <i>w, sh</i>	273 <i>w, sh</i>	279 <i>s, sh</i>	628 <i>m, sh</i>
		$\nu_{as}(ML')^{***}$	$\nu_4(ML')$ stretch***	316 <i>vs, b</i>	310 <i>vs, b</i>	506 <i>vs</i>	640 <i>s</i>
A_2	—	—	—	—	—	—	—
B_1	Ra	$\nu_{as}(ML_2)$	$\nu_5(ML_4)$ square stretch	—	—	—	—
		$\delta(ML_2)$	$\nu_6(ML_4)$ out of plane deform.	—	—	—	—
B_2	Ra	$\gamma(ML_2)$	$\nu_7(ML_4)$ in plane deform.	—	—	—	—
E	IR, Ra	$\nu_{as}(ML_4)$	$\nu_8(ML_4)$ antisym. square stretch	330 <i>s, sh</i>	327 <i>s, sh</i>	305 <i>vs, b</i>	703 <i>vs, b</i>
		$\rho(MO)$	$\nu_9(MO)$ rocking	230 <i>m</i>	231 <i>s</i>	237 <i>m</i>	330 <i>m</i>
		$\delta(LMO)$	$\nu_{10}(LMO)$ deform.	218 <i>w</i>	217 <i>w</i>	215 <i>w</i>	231 <i>w</i>
		$\rho(ML')$	$\nu_{11}(ML_5)$ rocking	n.o.	n.o.	n.o.	272 <i>s</i>
		Combination bands	$2\nu_1$				1337 <i>w</i>
							1405 <i>m</i>
							1915 <i>m</i>

*Assignments employed in the present paper; ** Assignments employed in papers [65-67]

*** For compound $Cs_2[ReOCl_4F]$ this band corresponds to $\nu(ReF)$.

and strong bands at 316, 310 and 305 cm^{-1} for rhenium compounds result most certainly from overlapping of ν_2 and ν_1 or ν_2 and ν_8 in the latter case. The bands found at about 275 cm^{-1} in the spectra of rhenium complexes result from the deformation vibration of the $ReCl_4$ group and correspond most likely to $\nu_2(E_g)$ for the $ReCl_6^-$ anion. The weak band at 483 cm^{-1} appears in the region deprived of the $\nu(ReCl)$, $\nu(ReF)$ and $\nu(ReO)$ frequencies. This is a combination band: $\delta(ClReO) + \nu(ReCl_4)$.

The band assignment for the osmium oxycompound was made on the basis of the spectrum of gaseous OsF_6 published by Weinstock *et al.* [68]. The spectrum exhibits two bands, $\nu_3(F_{1u})$ 720 cm^{-1} and $\nu_4(F_{1u})$ 268 cm^{-1} , and a number of combination bands. The band frequencies are consistent with those observed by us for $OsOF_5$.

The $\nu(M=O)$ frequencies are observed for all compounds in Table VII over the 950-995 cm^{-1} region.

Ruthenium does not form any such compounds.

B. The MO_2L_4 type compounds

This type of compounds will be discussed on the basis of infra-red spectra of rhenium, ruthenium and osmium complexes with changing ligands. This system has two possible isomorphous modifications — cis compound with C_{2v} symmetry and trans compound with D_{4h}

Normal vibrations of the MO_2L_4 system

Isomer	Symmetry	Species	Activity		Number of bands	Type of normal vibration	Number of stretch. vibr. in IR	
			IR	Ra			$\nu(\text{M}=\text{O})$	$\nu(\text{ML})$
cis	C_{2v}	A_1	a	p	6	$\nu_s(\text{MO}_2), \delta(\text{MO}_2), \nu_s(\text{ML}_2), \nu_s(\text{ML}'_2), \delta(\text{ML}_2), \delta(\text{ML}'_2)$	1	2
		A_2	ia	dp	2	$\tau(\text{MO}_2), \tau(\text{ML}_2)$	—	—
		B_1	a	dp	3	$\nu_{as}(\text{MO}_2), \nu_{as}(\text{ML}_2), \delta(\text{LMO})$	1	1
		B_2	a	dp	4	$\gamma(\text{MO}_2), \nu_{as}(\text{ML}'_2), \gamma(\text{ML}_2), \rho(\text{ML}'_2)$	0	1
trans	D_{4h}	A_{1g}	ia	p	2	$\nu_s(\text{ML}_4), \nu_s(\text{MO}_2)$	—	—
		A_{1u}	a	f	0	—	—	—
		A_{2g}	ia	p	0	—	—	—
		A_{2u}	a	f	2	$\gamma(\text{ML}_4), \nu_{as}(\text{MO}_2)$	1	0
		B_{1g}	ia	p	1	$\delta(\text{ML}_4)$	—	—
		B_{1u}	a	f	0	—	—	—
		B_{2g}	ia	p	1	$\nu_s(\text{ML}_2)$	—	—
		B_{2u}	a	f	1	$\tau(\text{ML}_2)$	0	0
		E_g	ia	dp	1	$\delta(\text{MO}_2)$	—	—
		E_u	a	f	3	$\nu_{as}(\text{ML}_2), \delta(\text{ML}_2), \delta(\text{MO}_2)$	0	1

a - active, ia - inactive, p - polarized, dp - depolarized, f - forbidden transitions

TABLE IX

$\text{Cs}[\text{Re}(\text{CN})_6] \cdot \text{H}_2\text{O}$	$\text{Y}[\text{Re}(\text{CN})_6] \cdot \text{H}_2\text{O}$	$\text{K}_3[\text{ReO}_2(\text{CN})_4] \cdot \text{H}_2\text{O}$	Assignment [54, 69-71]
3550 m, vb	3568 m, vb	3550 w	$\nu(\text{OH})$
		3380 m	
		2120 vs	
2152 vs	2155 vs	2094 s, sh	$\nu(\text{CN})$
		2079 s	
1635 m	1635 m	1635 m	$\delta(\text{HOH})$
—	—	775 vvs, b	$\nu_{as}(\text{ReO}_2) A_{2u}$
442 w, sh	422 m	475 s	$\delta(\text{OReC})$ and $\nu(\text{ReC})$
		469 s	
424 m	407 s	435 m	$\nu(\text{ReC})$
406 w, sh	396 m	412 w	$\nu(\text{ReC})$
337 vs	350 vs	341 vs	$\delta(\text{ReCN})$
—	—	252 s	$\delta(\text{ReO}_2) E_u$

symmetry. Table VIII contains the normal vibrations of such systems determined on the basis of the group theory.

According to this table, it is rather easy to distinguish between the cis- and trans-isomer, since the trans compound exhibits one $\nu_{as}(\text{MO}_2)$ band in the infra-red, while the cis-compounds

TABLE X

en	[ReO ₂ en ₂]Cl	[Re(OH) ₂ en ₂]Cl ₃	[Re(OH) ₂ en ₂]F ₃	[ReO(OH) en ₂]Cl ₂	[ReOCl ₂ en]	[Re ₂ O ₃ en ₂ Cl ₄]	Assignments	
—	—	3400 <i>s, b</i>	3400 <i>s, vb</i>	3380 <i>vs, b</i>	—	—	$\nu(\text{OH})$	
3348 <i>vs</i>	3212 <i>s, sh</i>	3352 <i>vs, b</i>	3270 <i>vs</i>	3164 <i>vs</i>	3265 <i>vs, sh</i>	3272 <i>s</i>	$\nu_{23} B_2$	
3270 <i>vs</i>	3166 <i>vs</i>		3208 <i>vs</i>	3124 <i>vs, sh</i>	3230 <i>vs</i>	3228 <i>vs</i>	$\nu_{17} A_1$	
3191 <i>s</i>	3084 <i>vs</i>	3129 <i>vs, b</i>	3116 <i>s</i>	3083 <i>s, sh</i>	3180 <i>vs</i>	3201 <i>vs</i>	$\nu_{17} B_1$	
				3040 <i>vs</i>	3100 <i>vs</i>	3136 <i>s</i>		
2924 <i>vs</i>	2985 <i>s</i>	2975 <i>vs</i>	2993 <i>m</i>	2970 <i>vs</i>	2949 <i>m</i>	2948 <i>m</i>	$\nu_{24} B_2$	
2852 <i>vs</i>	2958 <i>s</i>		2950 <i>s</i>	2949 <i>m</i>	2888 <i>w</i>		$\nu_{18} B_1$	
2738 <i>m</i>	2933 <i>s</i>	2945 <i>vs</i>	2922 <i>s</i>	2882 <i>m</i>		2887 <i>w</i>	$\nu_{11} A_2$	
2682 <i>w, sh</i>	2886 <i>s</i>	2608 <i>w</i>	2852 <i>s</i>	2832 <i>w</i>			$\nu_2 A_1$	
	2520 <i>w</i>	2422 <i>w</i>		2418 <i>m</i>	2494 <i>w</i>		Overtone and combination bands of ethylenediamine	
	2360 <i>w</i>	2355 <i>w</i>	2393 <i>w</i>					
	2315 <i>w</i>	2308 <i>w</i>		2325 <i>w</i>	2315 <i>w</i>	2326 <i>w</i>		
	2163 <i>w</i>		2200 <i>w</i>		2250 <i>m</i>	2240 <i>w</i>		
	2100 <i>w</i>	2110 <i>w</i>	2113 <i>w</i>	2142 <i>w</i>	2109 <i>w</i>	2108 <i>w</i>		
			1690 <i>w</i>		1890 <i>w</i>	1885 <i>w</i>		
1595 <i>vs</i>	1600 <i>s</i>	1572 <i>vs</i>	1563 <i>vs</i>	1577 <i>m, sh</i>	1563 <i>vs</i>	1579 <i>vs</i>	$\nu_3 A_1$	
		1562 <i>s, sh</i>		1573 <i>vs</i>		1562 <i>vs</i>	$\delta(\text{NH}_2)$	
		1542 <i>m</i>	1542 <i>s, sh</i>	1560 <i>m, sh</i>		1555 <i>vs</i>		
1457 <i>m</i>	1455 <i>m</i>	1462 <i>s</i>	1452 <i>vs</i>	1460 <i>m, sh</i>	1463 <i>s</i>	1462 <i>s</i>	$\nu_4 A_1$	
1448 <i>m, sh</i>	1443 <i>vs</i>	1450 <i>vs</i>	1445 <i>s</i>	1454 <i>s</i>	1456 <i>s</i>	1457 <i>s</i>	$\nu_{26} B_2$	
	1400 <i>w</i>				1400 <i>w</i>	1395 <i>w</i>	combination band of en	
1366 <i>m, sh</i>	1378 <i>vs</i>	1363 <i>s</i>	1368 <i>w</i>	1362 <i>s</i>	1384 <i>vs</i>	1364 <i>w</i>	$\nu_{19} B_1$	
1355 <i>m</i>					1362 <i>s</i>		$\omega(\text{CH}_2)$	
1307 <i>m</i>	1328 <i>s</i>	1331 <i>m</i>	1316 <i>s</i>	1323 <i>m</i>	1314 <i>s</i>	1315 <i>m</i>		
		1302 <i>vs</i>		1306 <i>vs</i>			$\nu_{27} B_2$	
	1124 <i>s</i>	1123 <i>s</i>	1148 <i>vs</i>	1129 <i>s</i>	1138 <i>vs</i>	1140 <i>vs</i>	$\nu(\text{CH}_2), \nu(\text{NH}_2)$	
	1292 <i>vs</i>	1286 <i>m</i>	1293 <i>vs</i>	1281 <i>m</i>	1291 <i>vs</i>	1290 <i>vs</i>		
	1242 <i>vs</i>	1250 <i>vs</i>		1243 <i>vs</i>	1275 <i>s</i>			
	1225 <i>m, sh</i>	1220 <i>m</i>	1201 <i>m</i>		1204 <i>s</i>	1203 <i>s</i>		
1175 <i>w, b</i>	1163 <i>vs</i>	1172 <i>vs</i>		1166 <i>vs</i>	1150 <i>vs</i>	1190 <i>m, sh</i>		$\nu_{20} B_1$
1097 <i>m</i>	1106 <i>s</i>		1109 <i>w</i>	1110 <i>s</i>	1110 <i>s</i>	1111 <i>m</i>		$\nu_6 A_1$
1053 <i>m</i>	1058 <i>vs</i>	1052 <i>vs</i>	1048 <i>vs</i>	1056 <i>vs</i>	1050 <i>vs</i>	1052 <i>vs</i>	$\nu_{28} B_2$	
	1017 <i>s</i>						$\nu(\text{NH}_2)$	
	1007 <i>vs</i>	1003 <i>vs</i>	998 <i>vs</i>	1001 <i>vs, sh</i>	1004 <i>m</i>	1005 <i>m</i>		
974 <i>s, sh</i>	1000 <i>vs</i>	983 <i>s</i>	994 <i>vs</i>	999 <i>vs</i>	983 <i>vs</i>	982 <i>s</i>	$\nu_7 A_1$	
				981 <i>vs</i>	970 <i>vs</i>	935 <i>m</i>	$\nu(\text{Re} = \text{O})$	
895 <i>vs</i>	898 <i>m</i>			889 <i>m</i>	887 <i>m</i>	890 <i>m, sh</i>	$\nu_8 A_1$	
	882 <i>m</i>	882 <i>m</i>	867 <i>m</i>	883 <i>w</i>	873 <i>s</i>	875 <i>s</i>		
					864 <i>m</i>		$\rho(\text{CH}_2)$	
	819 <i>vs, b</i>					800 <i>w, sh</i>	$\nu_{as}(\text{ReO}_2)$	
820 <i>vs</i>	815 <i>vs, sh</i>	802 <i>s</i>	818 <i>w</i>	820 <i>w</i>	821 <i>w</i>	809 <i>w, sh</i>	$\nu_{14} A_2$	
	750 <i>vs</i>	775 <i>w</i>	741 <i>s</i>	773 <i>m</i>	744 <i>vs</i>	760 <i>s, sh</i>	$\nu_{21} B_1$	
						730 <i>vs, sh</i>	$\nu_{as}(\text{ReORe})$	
	723 <i>vs</i>	731 <i>m</i>	741 <i>s</i>		700 <i>s</i>	724 <i>vs</i>	$\rho(\text{NH}_2)$	
	693 <i>vs</i>	627 <i>m</i>	700 <i>w</i>	629 <i>vs</i>	665 <i>w</i>	706 <i>vs, sh</i>		

Table X (continued)

en	[ReO ₂ en ₂]Cl	[Re(OH) ₂ en ₂]Cl ₃	[Re(OH) ₂ en ₂]F ₃	[ReO(OH) en ₂]Cl ₂	[ReOCl ₃ en]	[Re ₂ O ₃ en ₂ Cl ₄]	Assignments
	—	571 <i>s</i>	554 <i>s</i>	565 <i>s</i>	—	—	$\nu(\text{Re-OH})$
	556 <i>w</i>						
	568 <i>w</i>	557 <i>m</i>	542 <i>s</i>	558 <i>s, sh</i>	557 <i>s</i>	550 <i>m</i>	$\nu(\text{ReN})$ with $\varrho(\text{NH}_2)$
510 <i>m</i>	489 <i>s</i>	514 <i>s</i>	502 <i>vs</i>	517 <i>vs</i>	515 <i>s</i>	511 <i>m</i>	$\nu_{30} B_2$ $\varrho(\text{NH}_2)$ or $\delta(\text{NCCN})$
475 <i>w</i>	446 <i>w</i>	448 <i>s</i>	438 <i>s</i>	468 <i>w</i>	442 <i>s</i>	441 <i>s</i>	$\nu_9 A_1$ } $\delta(\text{NCCN})$
	418 <i>w</i>			435 <i>s</i>			} $\nu(\text{ReN})$
366 <i>m, vb</i>	348 <i>vw</i>	335 <i>s</i>	329 <i>s</i>	337 <i>m</i>	336 <i>s</i>	338 <i>m</i>	$\nu_{22} B_1$ } NH_2 -torsion
	309 <i>m</i>	325 <i>m, sh</i>	317 <i>s</i>				} $\nu(\text{ReCl})$
	—	—	—	—	308 <i>vs</i>	305 <i>vs</i>	$\nu(\text{ReN})$ and
	291 <i>s</i>	303 <i>m, sh</i>	306 <i>m</i>	285 <i>m</i>	283 <i>vs, b</i>	291 <i>s</i>	$\delta(\text{NReN})$
	280 <i>m, sh</i>	273 <i>s</i>	266 <i>m</i>	273 <i>s</i>		281 <i>s</i>	$\delta(\text{NReN})$ and ring deform.
	229 <i>m, sh</i>		236 <i>w, sh</i>	248 <i>w, sh</i>	232 <i>s</i>	232 <i>m</i>	$\delta(\text{NReN})$ and ring deform.
	215 <i>s</i>			220 <i>m</i>	217 <i>s</i>	215 <i>m</i>	$\delta(\text{OReO}), \delta(\text{OReCl})$ or $\delta(\text{OReOH})$

should possess two bands resulting from the symmetric and asymmetric vibrations of the MO_2 group.

The vibrational spectra of cyanide rhenium complexes have been examined by several authors [54, 69, 70]. On the basis of these studies and assignments given by Nakamoto [71], we have described the bands for $[\text{Re}(\text{CN})_6]^-$ and $\text{K}_3[\text{ReO}_2(\text{CN})_4] \cdot \text{H}_2\text{O}$ (Table IX).

The spectrum of $\text{K}_3[\text{ReO}_2(\text{CN})_4] \cdot \text{H}_2\text{O}$ exhibits only one vibration of the ReO_2 group, which is evidence of trans configuration of the oxygens in the OReO system. This result confirms the structural X-ray analysis made earlier [72].

Another group of compounds examined in the present paper are the compounds of rhenium with ethylenediamine. The spectra of these compounds together with their assignments are given in Table X. The complexes of formulae $[\text{ReOCl}_3\text{en}]$ and $[\text{Re}_2\text{O}_3\text{en}_2\text{Cl}_4]$ will be discussed separately (pp 88 and 92), but, in order to eliminate the bands of ethylenediamine, it was necessary to enter all these spectra into one table. The spectrum of ethylenediamine is relatively complex over the entire region examined by us. In spite of this, it is not difficult to eliminate the bands resulting from this ligand. For comparison, we have also obtained the spectrum of ethylenediamine alone [73].

The changes in the spectrum of bounded ethyldiamine depending on structure enable certain conclusions to be drawn in determinations of the isomeric structure of the formed complex. The results of studies on a large number of cis- and trans-compounds enabled us to develop a general interpretation and classification of compounds where ethylenediamine appears as a ligand. According to these results:

— the ethylenediamine band $\delta(\text{NH}_2)$ at about 1600 cm^{-1} is split into a sharp doublet for the cis-compounds [74, 75];

TABLE XI

<i>py</i>	[ReO ₂ py ₄]Cl	[ReOCl ₃ py ₂]	[Re ₂ O ₃ py ₄ Cl ₄]	Assignment
	3400 <i>s, b</i>			$\nu(\text{OH})$
3077 <i>vs</i>		3099 <i>s</i>	3070 <i>vs</i>	$\nu_{20b} B_1$
3052 <i>vs</i>		3088 <i>m</i>		$\nu_{20a} A_1$
3032 <i>vs</i>	3040 <i>vs, vb</i>	3062 <i>s</i>	3064 <i>vs</i>	$\nu_{7b} B_1$
3024 <i>vs</i>				$\nu_{13} A_1$
3000 <i>s</i>				$\nu_2 A_1$
2910 <i>w</i>		2911 <i>w</i>	2913 <i>w</i>	
	2800 <i>m, b</i>			
		2456 <i>w</i>	2452 <i>w</i>	
1986 <i>w</i>	2015 <i>w</i>	1999 <i>w</i>	1995 <i>w</i>	Overtone and combination bands of pyridine
1922 <i>m</i>	1968 <i>vw</i>	1968 <i>w</i>	1968 <i>w</i>	
1872 <i>w</i>		1898 <i>w</i>		
		1815 <i>w</i>	1825 <i>w</i>	
	1642 <i>s, b</i>			$\delta(\text{HOH})$
1632 <i>m</i>	1631 <i>m, sh</i>		1633 <i>w</i>	combination bands of pyridine
1598 <i>vs</i>	1617 <i>s</i>	1610 <i>vs</i>	1606 <i>vs</i>	$\nu_{14} B_1$
1588 <i>vs</i>	1605 <i>vs</i>	1601 <i>s, sh</i>	1598 <i>m, sh</i>	$\nu_{8a} A_1$
1582 <i>vs</i>	1596 <i>m, sh</i>			$\nu_{8b} B_1$
1560 <i>w</i>	1561 <i>s</i>	1568 <i>s</i>	1573 <i>m</i>	Symmetry and in plane ring vibrations $\nu(\text{CC})$ and $\nu(\text{CN})$
1484 <i>vs</i>	1483 <i>vs</i>	1484 <i>vs</i>	1480 <i>vs</i>	
	1476 <i>vs, sh</i>	1475 <i>s, sh</i>	1473 <i>w, sh</i>	
1440 <i>vs</i>	1447 <i>vs</i>	1459 <i>vs</i>	1453 <i>vs</i>	$\nu_{19b} B_1$
1375 <i>m</i>	1384 <i>w</i>	1394 <i>vw</i>	1392 <i>vw</i>	$\nu_{14} B_1$
1357 <i>w</i>	1353 <i>s</i>	1353 <i>s</i>	1351 <i>m</i>	$\nu_{6a} + \nu_{10b}$
	1233 <i>s</i>	1247 <i>vs</i>	1241 <i>m</i>	In plane antisym. ring py vibr. $\nu(\text{CC})$ and $\nu(\text{CN})$
	1223 <i>s</i>			
1218 <i>vs</i>	1218 <i>vs</i>	1210 <i>vs</i>	1205 <i>vs</i>	$\nu_{9a} A_1$
	1163 <i>m</i>			
1148 <i>vs</i>	1149 <i>s</i>	1152 <i>s</i>	1142 <i>s</i>	$\nu_{15} B_1$
	1096 <i>w</i>	1094 <i>w</i>		(CH) deform.
	1075 <i>s, sh</i>			
1070 <i>vs</i>	1069 <i>vs</i>	1067 <i>vs</i>	1068 <i>vs</i>	$\nu_{17a} A_2$
	1063 <i>vs</i>			
1033 <i>vs</i>	1051 <i>s</i>	1050 <i>s</i>	1048 <i>s</i>	$\nu_{12} A_1$
	1048 <i>s</i>	1017 <i>vs</i>		Sym. ring pyridine vibr.
992 <i>vs</i>	1012 <i>s</i>	1012 <i>s, sh</i>	1015 <i>m</i>	
		1005 <i>m</i>		
	—	971 <i>vs, b</i>	949 <i>s</i>	$\nu(\text{Re} = \text{O})$
945 <i>w</i>	956 <i>m</i>	943 <i>vs</i>	938 <i>m</i>	$\nu_5 B_2$
	912 <i>w</i>	923 <i>w</i>	920 <i>w</i>	Antisym. out of plane (CH) vibr. combination band of pyridine
885 <i>w</i>	883 <i>m</i>	860 <i>m</i>	864 <i>m</i>	
	822 <i>vs, b</i>	—	803 <i>vw</i>	$\nu_{18a} A_1$
748 <i>vs</i>	785 <i>vs</i>	759 <i>vs</i>	761 <i>vs</i>	$\nu_4 B_2$
	770 <i>vs</i>			Antisym. out of plane ring vibr.
700 <i>vs</i>	704 <i>vs</i>	700 <i>w</i>	710	
	693 <i>vs</i>	682 <i>vs, b</i>	\updownarrow <i>vs</i>	$\nu_{11} B_2$
676 <i>m, sh</i>	665 <i>vw, sh</i>	669 <i>m, sh</i>	675 <i>vb</i>	B_1
				$\nu_{6b} B_1$

Table XI (continued)

<i>py</i>	[ReO ₂ py ₄]Cl	[ReOCl ₂ py ₂]	[Re ₂ O ₃ py ₄ Cl ₄]	Assignment
603 <i>vs</i>		651 <i>vs</i>	649 <i>m</i>	$\nu_{6a} A_1$
	473 <i>m</i>	648 <i>vs</i>		
	466 <i>m</i>	455 <i>vs</i>	457 <i>s</i>	} $\nu_{16a} A_1$ } Ring pyridine vibr.
407 <i>vs, b</i>	397 <i>w</i>			
	354 <i>m, b</i>	330 <i>vs</i>	328 <i>s</i>	} $\nu_{16b} B_1$ }
	—	321 <i>vvs</i>	310 <i>vvs</i>	$\nu(\text{ReCl})$
	286 <i>s</i>	298 <i>s, sh</i>	304 <i>s, sh</i>	} $\nu(\text{ReN})$ and $\delta(\text{NReN})$
	277 <i>s, sh</i>	271 <i>s</i>	272 <i>s</i>	
		263 <i>s</i>		
	230 <i>s</i>	235 <i>m</i>	234 <i>m</i>	} $\delta(\text{OReO}), \delta(\text{OReCl}), \delta(\text{NReN})$
	220 <i>s</i>	214 <i>m</i>	220 <i>m</i>	

— over the 1130–1150 cm⁻¹ region — $\omega(\text{NH}_2)$ the cis-isomers exhibit two bands while the trans-compound only one [76];

— over the 870–900 cm⁻¹ region — $\rho(\text{CH}_2)$ the cis-isomers exhibit a medium intensity doublet while the trans-compounds shows a single band [75, 77];

—the cis-isomers exhibit four bands over the region 400–600 cm⁻¹ while the trans compounds have two or three bands [78].

On the basis of these criteria the compounds examined by us may be found to possess a trans configuration, although in some cases splitting of certain bands is observed, due to the crystal effect, and a lowering of symmetry. The 1550–1600 cm⁻¹ band splitting in [Re₂O₃en₂Cl₄] and the doublets over the 870–900 cm⁻¹ region for the compounds of lower symmetry are particularly typical. The compound [ReO₂en₂]Cl exhibits a broad band with a characteristic doublet structure at about 820 cm⁻¹. This band is formed by overlapping of $\nu_{as}(\text{ReO}_2)$ and $\rho(\text{CH}_2)$. The deformation vibration of the ReO₂ group, $\delta(\text{OReO})$, is observed at 215 cm⁻¹.

The spectra of similar compounds of rhenium with pyridine are shown in Table XI. As previously, the table comprises the spectra of all compounds and also for comparison the pyridine spectrum.

The assignment of bands resulting from pyridine was based on papers published by Wilmshurst, Bernstein [79] and Kline, Turkevich [80]. The spectral characteristic, shifts and band intensities of the pyridine ligand agree with those observed by Greenwood [81] and Gill [82] for complexed pyridine. The spectrum of [ReO₂py₄]Cl exhibits a broad, strong band at 822 cm⁻¹ which results from $\nu_{as}(\text{ReO}_2)$. The absence of any band at about 890 cm⁻¹, corresponding to $\nu_s(\text{ReO}_2)$, is evidence of a trans configuration of the OReO group and D_{4h} symmetry. This spectrum exhibits two strong absorption peaks at about 225 cm⁻¹. The 220 cm⁻¹ band is most probably due to the deformation vibrations of the ReO₂ group, while the band at 230 cm⁻¹ is related to the $\delta(\text{NReN})$ frequency.

The next group of complex compounds of a MO_2L_4 type which have been investigated in the present work are the osmium compounds. Their spectra together with assignments are presented in Table XII.

All the osmium compounds examined by us over the 799–843 cm^{-1} region have a very strong band due to the asymmetric stretch of the $OOsO$ system belonging to the A_{2u} species. Meanwhile, almost all complexes do not exhibit any $\nu_s(OsO_2) - A_{1g}$ bands at about 890 cm^{-1} . This is evidence of a trans configuration of the OsO_2 group oxygens and D_{2h} symmetry. The compounds, which are recorded in the table as $K_2[OsO_2(OH)_2(NO_2)_2]$ and $K_2[OsO_2(OH)_2(C_2O_4)]$, for which the symmetric stretching vibrations $\nu_s(OsO_2)$ become active, yielding the bands of medium intensity at 899 and 905 cm^{-1} , respectively, are exceptions. For the first compound, the band at about 800 cm^{-1} has a doublet structure consisting of a strong absorption peak at 799 cm^{-1} and a shoulder at 820 cm^{-1} . Besides this, two new bands appear which are not exhibited by the nitrite complex $K_2[OsO_2(NO_2)_4]$. These bands occur at 530 and 245 cm^{-1} . Similar results have been obtained for the oxalate compound (Table XII). Atovmyan has suggested [83] that the osmium compounds reported by Wintrebert [34] as $[OsO_3X_2]^-$ or $[OsO_2(OH)_2X_2]^-$ are binuclear complexes with

a double $\mu\mu'$ -oxy bridge. Such $M \begin{array}{c} O \\ \diagdown \quad \diagup \\ M \end{array}$ system with $D_{2h}(V_h)$ symmetry should be expected

to exhibit three infra-red bands belonging to the species B_{1u}, B_{2u}, B_{3u} which appear in the regions where the osmium compounds exhibit new bands [84]. To these complexes most probably the formulae should be assigned: $K_4[Os_2O_6(NO_2)_4]$ and $K_4[Os_2O_6(C_2O_4)_2]$. Meanwhile, during the $\mu\mu'$ -oxy bridge formulation, the linear trans bond $OOsO$ becomes bent, what results in activation of the $\nu_s(OsO_2)$ vibrations.

The assignment of bands resulting from complex ligands [$\nu_1, \nu_2, \text{etc.}$, for $C_2O_4^{=}$, NO_2^- , NH_3 , etc.] was made on the basis of results reported by Nakamoto [71].

The deformation $\delta(OsO_2)$ vibrations belonging to the E_u species absorb over the 270–310 cm^{-1} range.

The last of the three heavy elements examined by us — ruthenium, also forms several compounds where the RuO_2 group appears. The spectra of these compounds are shown in Table XIII. For comparison, the spectra of several hydroxy complexes of ruthenium are shown in this table. The $\nu(M-OH)$ vibrations will be discussed later.

Similarly as in osmium and ruthenium compounds, the spectra of ruthenium oxy-complexes (Table XIII) only exhibit bands resulting from the asymmetric $\nu_{as}(RuO_2)$ vibrations, what suggests the trans configuration of the ruthenium di-oxy compounds. The deformation vibrations of the $ORuO$ group absorb over the frequency range corresponding to the $\delta(OOsO)$ frequencies, that is 295–309 cm^{-1} . The complex $[RuO_2(OH)_2(NH_3)_2]$ probably has a binuclear structure with a $\mu\mu'$ -oxy bridge. It should be then formulated as $[Ru_2O_6(NH_3)_4]$, like the osmium compounds discussed previously. Such a formulation is indicated by the absence

of the $\delta(RuOH)$ and $\nu(OH)$ bands. On the other hand, the bands related to the $Ru \begin{array}{c} O \\ \diagdown \quad \diagup \\ Ru \end{array}$ group vibrations appear in turn at 830(B_{3u}), 490(B_{2u}) and 200(B_{1u}) cm^{-1} . Bending of the

TABLE XII

Compound	$\nu_{as}(\text{OsO}_2)$ A_{2u}	$\nu_s(\text{OsO}_2)$ A_{1g}	$\delta(\text{OsO}_2)$ E_u	Other bands																						
				$\nu_{as}(\text{OsO}_2)$ E_u	$\nu_{as}(\text{NO}_2)$	$\nu_s(\text{NO}_2)$	$\delta(\text{ONO})$	$\rho_w(\text{NO}_2)$	$\nu(\text{OsN})$	$\delta(\text{NO}_s\text{N})$	ν_{7u}	ν_{7g}	ν_{1u}	ν_{1g}	ν_{2u}	ν_{2g}	ν_{3u}	ν_{3g}	ν_{4u}	ν_{4g}	ν_{5u}	ν_{5g}	ν_{6u}	ν_{6g}		
$\text{K}_2[\text{OsO}_2\text{Cl}_4]$ $(\text{NH}_4)_2[\text{OsO}_2\text{Cl}_4]$ $\text{C}_2\text{O}_2[\text{OsO}_2\text{Cl}_4]$ $\text{K}_2[\text{OsO}_2\text{Br}_4]$ $(\text{NH}_4)_2[\text{OsO}_2\text{Br}_4]$ $\text{K}_2[\text{OsO}_2(\text{OH})_4]$	838 vs	—	309 s	315 vs — $\nu_{as}(\text{OsCl}_2)E_u$; 298 m — $\gamma(\text{OsCl}_4)A_{2u}$; 202 w — $\delta(\text{OsCl}_2)E_u$	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	
	841 vs	—	304 vs	312 vs — $\nu_{as}(\text{OsCl}_2)E_u$; 295 m — $\gamma(\text{OsCl}_4)A_{2u}$; 205 w — $\delta(\text{OsCl}_2)E_u$	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
	835 vs	—	307 s	310 vs — $\nu_{as}(\text{OsCl}_2)E_u$; 293 m — $\delta(\text{OsCl}_4)A_{2u}$; 200 w — $\delta(\text{OsCl}_2)E_u$	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
	843 vs	—	292 s	224 m — $\nu_{as}(\text{OsBr}_2)E_u$	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
	839 vs	—	290 s	228 m — $\nu_{as}(\text{OsBr}_2)E_u$	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
804 vs	—	297 s	297 s	3280 m — $\nu(\text{OH})$; 1065 m — $\delta(\text{OsOH})$; 448 s — $\nu(\text{OsOH})$; 239 w — $\delta(\text{HO—Os—OH})$	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
$\text{K}_2[\text{OsO}_2(\text{OH})_2(\text{NO}_2)_2]$	843 vs, b	889 m	288 w	$\nu_{B_{3u}}(\text{Os}_2\text{O}_2)$	$\nu_{B_{3g}}(\text{Os}_2\text{O}_2)$	$\nu_{B_{1u}}(\text{Os}_2\text{O}_2)$	$\nu_{as}(\text{NO}_2)$	$\nu_s(\text{NO}_2)$	$\delta(\text{ONO})$	$\rho_w(\text{NO}_2)$	$\nu(\text{OsN})$	$\delta(\text{NO}_s\text{N})$	260 m													
				829 m, sh	530 w	243 m, b	1385 vs	1333 m 1345 s	833 m 825 m	635 m 617 m 558 m	362 m															
$\text{K}_2[\text{OsO}_2(\text{NO}_2)_4]$	841 vs	—	285 m	—	—	—	1381 vs	1331 s 1352 s	831 m 818 m	628 m 620 m 560 m	365 m	255 m														
$\text{K}_2[\text{OsO}_2(\text{OH})_2(\text{C}_2\text{O}_4)]$ $\text{K}_2[\text{OsO}_2(\text{C}_2\text{O}_4)_2]$ $\text{C}_2\text{O}_2[\text{OsO}_2(\text{C}_2\text{O}_4)_2]$ $(\text{NH}_4)_2[\text{OsO}_2(\text{C}_2\text{O}_4)_2]$	820 s, sh	905 m	303 m	$\nu_{B_{3u}}(\text{Os}_2\text{O}_2)$	$\nu_{B_{3g}}(\text{Os}_2\text{O}_2)$	$\nu_{B_{1u}}(\text{Os}_2\text{O}_2)$	ν_{7u}	ν_{7g}	ν_{1u}	ν_{1g}	ν_{2u}	ν_{2g}	ν_{3u}	ν_{3g}	ν_{4u}	ν_{4g}	ν_{5u}	ν_{5g}	ν_{6u}	ν_{6g}	ν_{11u}	ν_{11g}	ν_{10u}	ν_{10g}	ν_{12u}	ν_{12g}
				799 vs, b	503 m	240 m	1702 vs	1689s 1660s	1365s 1217 m	881s	815 m	522 m	468 w	405 w	380 w	325 m										
				—	—	—	1709 vs	1685s 1665s	1360s 1212 m	885s	820 m	552 m	470 w	420 w	370 w	330 m										
				—	—	—	1705 vs	1691s 1659s	1355s 1215 m	887s	820 m	553 m	475 w	415 w	375 w	332 m										
837 vs	—	—	290 m	—	—	—	1708 vs	1687s 1658s	1360s 1214 m	883s	824 m	550 m	482 w	411 w	384 w	340 m										

$K_2[OsO_2(CN)_4]$	830 <i>vs</i>	—	282 <i>s</i>	$\left. \begin{array}{l} 2145 \text{ vs} \\ 2080 \text{ s} \end{array} \right\} -\nu(CN); 465 \text{ m}-\nu(OsC); 431 \text{ m}-\delta(OOsC); 360 \text{ vs}-\delta(OsCN)$
$Cs_2[OsO_2(CN)_4]$	836 <i>vs</i>	—	279 <i>m, b</i>	$\left. \begin{array}{l} 2138 \text{ vs} \\ 2091 \text{ s} \end{array} \right\} -\nu(CN); 449 \text{ m}-\nu(OsC); 425 \text{ m}-\delta(OOsC); 365 \text{ vs}-\delta(OsCN)$
$As_2[OsO_2(CN)_4]$	832 <i>vs</i>	—	275 <i>m, b</i>	$\left. \begin{array}{l} 2141 \text{ vs} \\ 2075 \text{ s, s, h} \end{array} \right\} -\nu(CN); 458 \text{ m}-\nu(OsC); 442 \text{ m}-\nu(OOsC); 353 \text{ vs}-\delta(OsCN)$
$[OsO_2(NH_2)_4]Cl_2$	828 <i>vs</i>	—	271 <i>m, b</i>	$\left. \begin{array}{l} 3250 \text{ vs, b}-\nu(NH_2); 1605 \text{ s}-\nu_d(NH_2); 869 \text{ s}-\rho_r(NH_2); 485 \text{ m} \\ 420w \end{array} \right\} -\nu(OsN); 255 \text{ s, b}-\delta(NO_sN)$
$[OsO_2(NH_2)_4](OH)_2$	831 <i>vs</i>	—	278 <i>m</i>	$\left. \begin{array}{l} 3480 \text{ m, b}-\nu(OH); 3265 \text{ vs, b}-\nu(NH_2); 1603 \text{ s}-\nu_d(NH_2); 874 \text{ s}-\rho_r(NH_2); 471 \text{ m} \\ 389 \text{ w} \end{array} \right\} -\nu(OsN); 251 \text{ s, b}-\delta(NO_sN)$
$[OsO_2(NH_2)_4]SO_4$	939 <i>vs</i>	—	285 <i>m</i>	$\left. \begin{array}{l} 3248 \text{ vs, b}-\nu(NH_2); 1608 \text{ s}-\nu_d(NH_2); 1120 \text{ s}-\nu_3(SO_4), 970 \text{ vw}-\nu_1(SO_4); 878 \text{ s}-\rho_r(NH_2); 625 \text{ s}- \\ \nu_4(SO_4); 464 \text{ m, 393 w}-\nu(OsN); 260 \text{ m, b}-\delta(NO_sN) \end{array} \right\}$

TABLE XIII

Compound	ν_{as} (RuO ₂)	δ (RuO ₂)	δ (RuOH)	ν (Ru— —OH)	ν (OH)	Other bands
C ₂ [RuO ₂ Cl ₄]	818 vs, b	305 m	—	—	—	325 s— ν_{as} (RuCl ₂) E _u ; 285 m— γ (RuCl ₄) A _{2u}
Rb ₂ [RuO ₂ Cl ₄]	815 vs, b	301 m	—	—	—	318 s— ν_{as} (RuCl ₂) E _u ; 281 m— γ (RuCl ₄) A _{2u}
Cs ₂ [RuO ₂ Br ₄]	824 s, b	309 m	—	—	—	250 s— ν_{as} (RuBr ₂) E _u ; 218 m— γ (RuBr ₄) A _{2u}
[As(phen) ₄] ₂ [RuO ₂ Br ₄]	814 s, b	298 m	—	—	—	248 s— ν_{as} (RuBr ₂) E _u ; 212 m— γ (RuBr ₄) A _{2u}
[Asphen ₄] ₂ [RuO ₂ (SO ₄) ₂]	807 s, b	295 m	—	—	—	1125 m } — ν_3 (SO ₄); 975 m— ν_1 (SO ₄); 650 s, 615 s, 570 sh— ν_4 (SO ₄); 412 m— ν_2 (SO ₄) 1038 s }
Ag ₂ [Ru(OH)Cl ₄ (NO)]	—	—	919 m	528 s	3500 w	1885 s— ν (NO); 604 w— ν (Ru—NO); 360 w— δ (RuNO); 321 s— ν (RuCl ₂); 230 w } δ (ORuN) 208 m, sh } δ (ClRuN)
K ₂ [Ru(OH)(NO ₂) ₄ (NO)]	—	—	958 m	584 w	3525 m	1400 w } 835 w } 1872 vs— ν (NO); 1330 m } — ν (NO ₂); 830 s } — δ (NO ₂); 570 w— ω (NO ₂); 1305 sh } 818 w }
						628 m— ν (Ru—NO); 347 m— δ (RuNO); 335 s, 300 s, 271 s, 240 w— δ (NRuN) and δ (ORuN)
[RuO ₂ (OH) ₂ (NH ₃) ₂]*	795 s, b	305 m	—	—	—	ν_{B8u} } ν_{B2u} } ν_{B1u} } (Ru ₂ O ₂) } (Ru ₂ O ₂) } (Ru ₂ O ₂) } 830 m, sh } 490 s } 200 w } ν (NH) } ν (NO) } δ (NH ₃) } ν (Ru— —NH ₃) } δ (NRuO) } 3250 s } — } 1560 m } 505 m } 272 m } 3128 s } — } 1341 w } 460 m } 251 m } 3245 s } 1885 vs } 1302 m } 500 w } 235 m, sh } 3150 vs } 1288 m } 473 m } 318 w } 1850 vs } 1570 m } 633 m } 271 m } 3131 s } 1345 w } 228 w } 325 vs } 821 m, sh } 1300 m } 465 m } 273 s } 210 v, sh }
[Ru(OH)(NH ₃) ₄ (NO)]Cl ₃	—	—	970 m	574 m	3450 m	
[Ru(OH)(NH ₃) ₄ (NO)]Br ₂	—	—	962 m	581 m	3425 m	

*In this case activities symmetric vibrations ν_5 (RuO₂): 820 m, sh.

linear ORuO bond in this compound activates the symmetric $\nu_s(\text{RuO}_2)$ vibration which appears at about 795 cm^{-1} .

Assuming the model of metal-oxygen interactions suggested for the vanadyl [85] and osmyl [86] complexes, it is possible to explain theoretically the appearance of the trans configuration in the dioxy-compounds of rhenium, osmium and ruthenium examined by us. We shall consider only the " $p_\pi-d_\pi$ " overlap ($2p$ orbitals of oxygen with free d orbitals of metal) since mainly these orbitals determine the arrangement of the oxygen atoms. The positions of ligands will be defined by the cartesian coordinates and then:

TABLE XIV

Positions of the oxygen

Symmetry	O ₁	Overlap	O ₂	Overlap
C_{2v}	O _x	$2p_y-d_{xy}$ $2p_z-d_{xz}$	O _y	$2p_x-d_{xy}$ $2p_z-d_{yz}$
D_{4h}	O _x ¹	$2p_y-d_{xy}$ $2p_z-d_{xz}$	O _x ²	$2p_y-d_{xy}$ $2p_z-d_{xz}$

If the oxygen atoms are in trans positions along the x axis, then the d_{xy} and d_{xz} orbitals will participate in the π bonding from the part of the metal. The d_{yz} orbital will be non-bonding for this symmetry. Next, for a cis configuration of the oxygens all three d_π orbitals of the metal participate in the bonding with the oxygen atom. Therefore, the d^2 electron metals (osmium-VI, rhenium-V and ruthenium-VI) form complex compounds of D_{4h} symmetry, since both d_π electrons can be placed in the non-bonding d_{yz} orbital which is advantageous for energy reasons. The C_{2v} symmetry is instead characteristic of the d^0 configuration, where both oxygens are in the cis position. With such symmetry all d_π orbitals participate in the π bonding with the oxygen atoms and, therefore, the total π bonding effect is higher than that for the trans structure of the complex. This results from the higher $\nu(\text{MO}_2)$ frequencies for the cis compounds with respect to those for the trans-isomers.

C. The $[\text{MO}(\text{OH})\text{L}_4]$ type compounds and hydroxy-compounds

Generally speaking, the hydroxy-compounds have three absorption ranges: $\nu(\text{OH})$ $3200-3500\text{ cm}^{-1}$, $\delta(\text{MOH})$ $800-1200\text{ cm}^{-1}$ and $\nu(\text{M}-\text{OH})$ $400-600\text{ cm}^{-1}$.

The only rhenium hydroxy-complexes examined by us are those with ethylenediamine (Table X). Absorption resulting from the $\nu(\text{OH})$ vibrations takes place at $3400-3450\text{ cm}^{-1}$. Complexed ethylenediamine has two weak bands of equal intensities over the $550-600\text{ cm}^{-1}$ region. Overlapping of these bands with the $\nu(\text{Re}-\text{OH})$ band results in strengthening of the band at higher frequencies. The $\nu(\text{Re}-\text{OH})$ frequency corresponds to the stretching vibration of the rhenium-oxygen bonding of a bond order 1. Ethylenediamine gives several bands over the $1000-1100\text{ cm}^{-1}$ region, and it was impossible to determine which of these bands is due to the deformation vibrations $\delta(\text{ReOH})$.

The $\nu(\text{Re}=\text{O})$ frequency for $[\text{ReO}(\text{OH})\text{en}_2]\text{Cl}_2$ is at 981 cm^{-1} . The deformation $\delta(\text{HO}-\text{Re}-\text{OH})$ frequency appears most probably at 220 cm^{-1} .

Analysis of spectral bands exhibited by osmium hydroxy-compound is less difficult (Table XII). The hydroxyl group vibrations absorb at frequencies $\nu(\text{Os}-\text{OH})$ 448, $\delta(\text{OsOH})$ 1065 and $\delta(\text{HO}-\text{Os}-\text{OH})$ 239 cm^{-1} .

Comparable data were obtained for the ruthenium hydroxy-compounds (Table XIII). The stretching vibration of a single ruthenium-oxygen bond absorbs at somewhat higher frequencies than the osmium compounds, namely at 528–584 cm^{-1} . The deformation $\delta(\text{RuOH})$ vibrations give the bands in the 919–970 cm^{-1} region.

The band assignment for nitrosyl and amino groups in the ruthenium hydroxy-compounds (Table XIII) was made on the basis of the results reported by Mercer [87], Gans [88], Allen [89, 90] *et al.*

D. The MO_3X_2 type compounds

This type of compounds will be discussed for the rhenium compounds only. Osmium and ruthenium do not form any complexes of such structure. According to Table V, the compounds $[\text{ReOCl}_3\text{X}_2]$ should exhibit a single $\nu(\text{Re}=\text{O})$ band and triplets $\nu(\text{ReCl})$ both for C_{2v} and C_s symmetry. The spectra obtained by us (Tables X and XI) contain the bands corresponding to the stretching $\nu(\text{Re}=\text{O})$ vibrations at 971 cm^{-1} for the pyridine complex and at 970 cm^{-1} for the ethylenediamine compound. In both cases a very complex spectral structure is observed in the 270–330 cm^{-1} region, where the $\nu(\text{ReCl})$ vibrations occur. This structure results from overlapping of $\nu(\text{ReCl})$ with $\nu(\text{ReN})$ and $\delta(\text{NReN})$.

E. The MO_3L_3 type compounds

Only two compounds of this type been examined by us: $\text{Cs}_2[\text{ReO}_3\text{Cl}_3]$ and $\text{Cs}[\text{OsO}_3\text{F}_3]$. For such systems the following table of normal frequencies may be set up:

TABLE XV

Normal vibrations of the MO_3L_3 system

Isomer	Symmetry	Species	Activity		Number of bands	Type of normal vibration	Number of stretching vibrations in IR	
			IR	Ra			$\nu(\text{MO})$	$\nu(\text{ML})$
cis	C_{3v}	A_1	a	p	4	$\nu_s(\text{MO}_3), \delta_s(\text{MO}_3), \nu_s(\text{ML}_3), \delta_s(\text{ML}_3)$	1	1
		A_2	ia	f	1	$\delta(\text{LMO})$	—	—
		E	a	p	5	$\nu_{as}(\text{MO}_3), \delta_{as}(\text{MO}_3), \nu_{as}(\text{ML}_2), \delta_{as}(\text{ML}_3), \delta(\text{LMO})$	1	1
trans	C_{2v}	A_1	a	p	6	$\nu_s(\text{MO}_2), \delta(\text{MO}_2), \nu(\text{MO}), \nu_s(\text{ML}_2), \delta(\text{ML}_2), \nu(\text{ML})$	2	2
		A_2	ia	dp	1	$\delta(\text{LMO})$	—	—
		B_1	a	dp	4	$\nu_{as}(\text{MO}_2), \delta(\text{MO}_2), \gamma(\text{ML}_2), \delta(\text{LMO})$	1	0
		B_2	a	dp	4	$\nu_{as}(\text{ML}_2), \delta(\text{ML}_2), \gamma(\text{MO}_2), \delta(\text{LMO})$	0	1

a - active, ia - inactive, p - polarized, dp - depolarized, f - forbidden transitions.

According to this table, the cis compound with C_{3v} symmetry should exhibit two stretching frequencies, metal-oxygen and metal-chlorine, while the trans compounds with C_{2v} symmetry exhibit three bands each. The spectra of these compounds together with their assignments are given in Table XVI.

TABLE XVI

$Cs_2[ReO_3Cl_3]$	$Cs[OsO_3F_3]$	Vibrational mode	Species of vibration
935 <i>s</i>	952 <i>s, b</i>	$\nu_s(MO_3)$	A_1
890 <i>vs, b</i>	915 <i>vs, b</i>	$\nu_{as}(MO_3)$	E
370 <i>s</i>	578 <i>s</i>	$\nu_s(ML_3)$	A_1
330 <i>m</i>	469 <i>s</i>	$\nu_{as}(ML_3)$	E
321 <i>vs</i>	348 <i>m</i>	$\delta(MO_3)$	A_1
315 <i>m, sh</i>	315 <i>m</i>	$\delta_{as}(MO_3)$	E
220 <i>vs</i>	215 <i>w</i>	$\delta(LMO)$	E

A comparison of Tables XV and XVI may suggest cis configuration of the rhenium compound and C_{3v} symmetry, since the band at 890 cm^{-1} , very strong and broad, is a clear doublet. C_{3v} symmetry is also indicated by the number of bands resulting from the rhenium-chlorine stretching frequencies. In order to obtain a full analysis and to confirm this structure a Raman spectrum is required, however. The two bands found in the $215\text{--}225\text{ cm}^{-1}$ region are due to the deformation frequencies of the ReO_3 group.

The osmium compound is also likely to have C_{3v} symmetry. Its spectrum agrees with the characteristic of normal vibrations for the cis system MO_3L_3 given in Table XV.

It seems, then, that the cis-structure of the trioxy compounds is characteristic of transition metals with a d^0 electron configuration in the complex. This becomes evident if the positions of oxygens with respect to the metal and the overlap of d_π -metal and p_π -oxygen orbitals (Table XVII) are defined.

TABLE XVII

Positions of the oxygen

Symmetry	O ₁	Overlap	O ₂	Overlap	O ₃	Overlap
C_{3v}	O _x	$2p_y-d_{xy}$ $2p_z-d_{xz}$	O _y	$2p_x-d_{xy}$ $2p_z-d_{yz}$	O _z	$2p_x-d_{xz}$ $2p_y-d_{yz}$
C_{2v}	O _x ¹	$2p_y-d_{xy}$ $2p_z-d_{xz}$	O _x ²	$2p_y-d_{xy}$ $2p_z-d_{xz}$	O _y	$2p_x-d_{xz}$ $2p_z-d_{yz}$

In the complexes of C_{2v} symmetry three d_π orbitals do not participate equally in the π bonding with oxygens. The d_{xy} orbital participates in the bonding with three ligands, the d_{xz} orbital with two ligands and the d_{yz} orbital with only one ligand. Hence, the latter orbital will be least antibonding, and its filling with one or two electrons will be energetically more advantageous than for C_{3v} symmetry, where the antibonding effect is higher. For C_{3v}

symmetry the bonding contributions of d_x orbitals are equal and are better utilized. Therefore, this symmetry is more convenient for the central ions of the d^0 configuration (Re—VII and Os—VIII). We have observed this in the rhenium (VII) and osmium (VIII) compounds which have C_{3v} symmetry.

F. Binuclear compounds

Rhenium, ruthenium and osmium readily form binuclear compounds in which oxygen forms a bridge bonding MOM between the metal atoms. The dimeric rhenium-IV and V complexes as well as osmium-IV and ruthenium-IV complexes are particularly stable. Oxidation state IV of rhenium is represented in our work by potassium and caesium oxychlorhenates and the compound $K_6[Re_2O_3(CN)_8] \cdot 4H_2O$. The spectra of these compounds together with their assignments are shown in Tables XVIII and XIX.

TABLE XVIII

$K_6[Re_2O_3(CN)_8] \cdot 4H_2O$	Assignment
3450 <i>m, vb</i>	$\nu(OH)$
2125 <i>s</i>	$\nu(CN)$
2080 <i>s, b</i>	$\delta(HOH)$
1620 <i>m</i>	$\nu(Re=O)$
912 <i>s</i>	$\nu_{as}(ReO_2)$
784 <i>s</i>	$\nu_{as}(ReORe)$
752 <i>s</i>	$\nu(ReC)$
474 <i>vs</i>	$\delta(OReC)$
462 <i>s</i>	$\delta(ReCN)$
335 <i>s</i>	$\delta(O_tReO_b)$
252 <i>m</i>	$\nu_s(ReORe)$
200 <i>vw</i>	

L' denotes a ligand in the trans-position with respect to the bridging oxygen. The notation in table refers to the isolated MO_bL_5 groups of C_{4v} symmetry (O_b — bridge oxygen) and MOM of $D_{\infty h}$ symmetry.

Rhenium-V of a d^2 electron configuration appears in binuclear compounds with ethylenediamine (Table X) and pyridine (Table XI) of formulae $[Re_2O_3en_2Cl_4]$ and $[Re_2O_3py_4Cl_4]$.

Considering the $[L_5MOML_5]^*$ type binuclear compounds as a "three-body" system, one should expect the vibrational spectra to exhibit three frequencies: $\nu_{as}(MOM)$, $\nu_s(MOM)$ and $\delta(MOM)$. In the angular bridge MOM of C_{2v} symmetry all three frequencies are both IR and Raman active. The symmetric stretching bridge vibrations absorb in the 400–550 cm^{-1} region, similarly as the compounds of chromium [91, 92], tin, germanium [93], arsenic and antimony [84]. Since no new bands have been observed to form over this region, this suggests a linear structure of the rhenium compounds examined by us. According to the selection rules, the linear nucleus MOM should exhibit only the asymmetric stretching frequencies, while $\nu_s(MOM)$ is only Raman active, giving the bands at about 200–250 cm^{-1} . Owing to some crystal effects however, this vibration becomes sometimes infrared active.

TABLE XIX

Compound	Cation	ν_{as} (MOM) $\sum_{u^+}(D_{\infty h})$	ν_s (MOM) $\sum_g^+(D_{\infty h})$	δ (LMO) $E(C_{4v})$	ν (OH)	δ (HOH)	Other bands
$\text{Re}_2\text{OCl}_{10}^{4-}$	K	855 <i>s</i>	200 <i>vw</i>	210 <i>w</i>	—	—	326 <i>s, sh</i> — $\nu_{as}(\text{ReCl}_4)$; 315 <i>vs, b</i> — $\nu_s(\text{ReCl}_4)$; 305 <i>vs, b</i> — $\nu_{as}(\text{ReCl}')$
	Cs	851 <i>s</i>	202 <i>vw</i>	210 <i>w</i>	—	—	322 <i>s, sh</i> — $\nu_{as}(\text{ReCl}_4)$; 310 <i>vs, b</i> — $\nu_s(\text{ReCl}_4)$ and $\nu_{as}(\text{ReCl}')$
$\text{Os}_2\text{OCl}_{10}^{4-}$	NH_4	845 <i>m</i>	—	220 <i>w</i>	3580 <i>m</i>	1625 <i>m</i>	310 <i>vs</i> — $\nu_{as}(\text{OsCl}_4)$; 304 <i>s</i> — — $\nu_s(\text{OsCl}_4)$; 273 <i>w</i> — $\nu_{as}(\text{OsCl}')$
	Y	838 <i>m</i>	—	225 <i>w</i>	3620 <i>m</i>	1638 <i>m</i>	319 <i>vs</i> — $\nu_{as}(\text{OsCl}_4)$; 309 <i>s</i> — — $\nu_s(\text{OsCl}_4)$; 281 <i>w</i> — $\nu_{as}(\text{OsCl}')$
$\text{Os}_2\text{OBr}_{10}^{4-}$	Cs	843 <i>m</i>	—	n.o.	3550 <i>m</i>	1620 <i>m</i>	205 <i>s</i> — $\nu_{as}(\text{OsBr}_4)$
	Y	845 <i>m</i>	—	n.o.	3480 <i>m</i>	1609 <i>m</i>	200 <i>s</i> — $\nu_{as}(\text{OsBr}_4)$
$\text{Os}_2\text{OI}_{10}^{4-}$	Cs	835 <i>m</i>	—	n.o.	3520 <i>m</i>	1600 <i>w</i>	
	Y	841 <i>m</i>	—	n.o.	3545 <i>m</i>	1605 <i>m</i>	
$\text{Os}_2\text{OCl}_6\text{Br}_4^{4-}$	Cs	848 <i>m</i>	205 <i>w</i>	210 <i>w</i>	3578 <i>m</i>	1630 <i>m</i>	310 <i>s</i> — $\nu_{as}(\text{OsCl}_4)$; 225 <i>s</i> — — $\nu_{as}(\text{OsBr}_2)$; 292 <i>s</i> — $\nu_s(\text{OsCl}_4)$; 270 <i>w</i> — $\nu_{as}(\text{OsCl}')$
	Y	846 <i>m</i>	204 <i>w</i>	215 <i>m, sh</i>	3600 <i>m</i>	1628 <i>m</i>	315 <i>s</i> — $\nu_{as}(\text{OsCl}_4)$; 290 <i>s</i> — — $\nu_s(\text{OsCl}_4)$; 275 <i>w</i> — $\nu_{as}(\text{OsCl}')$; 225 <i>s</i> — $\nu_{as}(\text{OsBr}_2)$
$\text{Os}_2\text{OCl}_8\text{I}_2^{4-}$	Cs	832 <i>m</i>	215 <i>m, sh</i>	225 <i>m</i>	3575 <i>m</i>	1630 <i>m</i>	318 <i>s</i> — $\nu_{as}(\text{OsCl}_4)$; 295 <i>m</i> — $\nu_s(\text{OsCl}_4)$
	Y	830 <i>m</i>	213 <i>m</i>	225 <i>m</i>	3520 <i>m</i>	1630 <i>m</i>	321 <i>s</i> — $\nu_{as}(\text{OsCl}_4)$; 298 <i>w</i> — $\nu_s(\text{OsCl}_4)$
$\text{Ru}_2\text{OCl}_{10}^{4-}$	K	885 <i>s</i>	—	n.o.	3480 <i>m</i>	1615 <i>m</i>	324 <i>vs</i> — ν_s and $\nu_{as}(\text{RuCl}_4)$; 289 <i>w</i> — $\nu_{as}(\text{RuCl}')$; 463 <i>m</i> — $2\nu_{as}(\text{RuORu})$
	Y	880 <i>s</i>	—	n.o.	3440 <i>m</i>	1612 <i>m</i>	322 <i>vs, b</i> — ν_s and $\nu_{as}(\text{RuCl}_4)$; 290 <i>w</i> — $\nu_{as}(\text{RuCl}')$; 465 <i>m</i> — $2\nu_s(\text{RuORu})$
$\text{Ru}_2\text{OBr}_{10}^{4-}$	K	858 <i>s</i>	—	n.o.	3480 <i>m</i>	1635 <i>m</i>	248 <i>m</i> — ν_s and $\nu_{as}(\text{RuBr}_4)$
	Y	861 <i>s</i>	—	n.o.	3510 <i>m</i>	1640 <i>m</i>	250 <i>m</i> — ν_s and $\nu_{as}(\text{RuBr}_4)$
$\text{Ru}_2\text{OCl}_8\text{Br}_2^{4-}$	Y	852 <i>m</i>	245 <i>m, b</i>	240 <i>w, sh</i>	3542 <i>m</i>	1642 <i>m</i>	334 <i>vs</i> — ν_{as} and $\nu_s(\text{RuCl}_4)$; 250 <i>m</i> — $\nu(\text{RuBr}')$; 278 <i>w</i> — $\nu_{as}(\text{RuCl}_2)$

where: Y = [As(phen)₄]; L' — ligand in trans position to the bridged oxygen atom.

This happens for some rhenium, osmium and ruthenium compounds (Table XIX), especially if the symmetry is disturbed by introducing another halogen ligand. A difference of about 120 cm^{-1} in the position of the $\nu_{as}(\text{ReORe})$ band in the cyanide (Table XVIII), pyridine (Table XI) and ethylenediamine (Table X) complexes with respect to other dimeric rhenium compounds (Table XIX) is anticipated and confirms the existence of the so called "electron-withdrawing" effect [2], consisting in a weakening of the bridge bonding ReORe in the linear system O-Re-O-Re-O. Owing to the electron attraction, a stretching action of the outer oxygens appears which leads to a decrease in the $\nu_{as}(\text{ReORe})$ frequency with respect to the μ -oxychlororhenates and binuclear thiocyanide rhenium compounds [94]. Meanwhile, the above compounds with abnormal $\nu_{as}(\text{ReORe})$ frequency exhibit a decrease in frequency and intensity of the $\nu(\text{Re}=\text{O}_t)$ vibration (O_t — terminal oxygen).

The vibrational spectra of binuclear osmium-IV and ruthenium-IV compounds also suggest that the MOM bridge has a linear arrangement and $D_{\infty h}$ symmetry, what confirms the results of structural X-ray analysis made earlier for the ruthenium compound [95]. The frequency ranges of asymmetric stretching vibrations of the bridge oxygen bonding ($830\text{--}885\text{ cm}^{-1}$) correspond to the frequencies given for rhenium compounds. Several dimeric compounds of osmium and ruthenium exhibit activation of their infra-red forbidden frequencies $\nu_3(\text{MOM})$ over the $200\text{--}250\text{ cm}^{-1}$ region. This happens for the compounds of a general formula $[\text{M}_2\text{OL}_x\text{L}'_{10-x}]^{4-}$ which have their symmetry disturbed by introducing a second halogen into the complex.

The deformation $\delta(\text{MOM})$ frequencies have not been observed by us since they are beyond the range of our instrument (below 200 cm^{-1}).

Force constants of the metal-oxygen bonds

On the basis of the above considerations one can compile the results related to the metal-oxygen bond frequency ranges (Table XX).

TABLE XX

Vibrational mode	$M = \text{Re}$	$M = \text{Os}$	$M = \text{Ru}$
$\nu(\text{M}=\text{O})$	912-995	952-960	—
$\nu_3(\text{MO}_2)$	890-912	889-905	—
$\nu_{as}(\text{MO}_2)$	775-835	799-843	795-824
$\nu(\text{M}-\text{OH})$	550-570	448-503	528-584
$\delta(\text{MO}_2)$	220-260	271-309	295-309
$\nu_{as}^-(\text{MOM})$	720-855	830-848	852-885
$\nu_3(\text{MOM})$	200-205	204-215	~235

From among the systems in the present work, the normal coordinate analysis was made till now for the molecules MOL_5 [C_{4v}], MO_2L_4 (C_{2v} and D_{4h}) [97] and $\text{MO}_n\text{L}_{4-n}$ (T_d [24], C_{3v} [96]). The normal coordinates are functions (sometimes complex ones) which comprise

the displacement coordinates of many or all atoms in the molecule. Both the kinetic and potential energies expressed in these Q_i coordinates contain only the square terms:

$$2T = \sum_{i=1}^{3n-6} \dot{Q}_i^2$$

$$2V = \sum_{i=1}^{3n-6} \lambda_i Q_i^2.$$

The frequency of the normal vibration is determined by the kinetic and potential energies of the system. The kinetic energy is determined by the masses of the individual atoms and their geometrical arrangement in the molecule. On the other hand, the potential energy arises from interaction between the individual atoms and is described in terms of the force constants. Since the potential energy provides valuable information about the nature of interatomic forces, it is highly desirable to obtain the force constants from the observed frequencies.

Using the internal coordinates R_i for a molecule, the potential energy is written:

$$2V = [\tilde{R}] [F] [R]$$

where $[F]$ is a matrix whose components are the force constants. The kinetic energy in terms of the same internal coordinates can be written as

$$2T = [\tilde{R}] [G^{-1}] [\dot{R}]$$

where $[G]$ is a matrix determined by the masses of the atoms and the geometry of the molecule.

If these two equations are combined with Newton's equation,

$$\frac{d}{dt} \left(\frac{\partial T}{\partial \dot{R}_k} \right) + \frac{\partial V}{\partial R_k} = 0$$

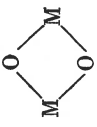
the following secular equation is obtained:

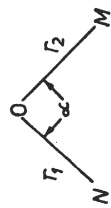
$$|[G] [F] - [E] \lambda| = 0.$$

Here, $[E]$ is the unit matrix and λ is related to the wave number $\tilde{\nu}$ by the relation $\lambda = 4\pi^2 c^2 \tilde{\nu}^2$. Such an analysis was made for the molecules described above. Since in most cases no X-ray data for the compounds studied by us are available, the force constants of the metal-oxygen bonds may be only approximately calculated. The secular equation usually has a block form in which each block is related to a definite species and a definite bonding. Moreover, almost the entire value of the stretching force constant and stretch-stretch interaction force constant is concentrated in the diagonal matrix terms. Hence, by selecting the corresponding terms of matrices $[G]$ and $[F]$ we have obtained a very good approximation for calculation of force constants f_r and f_{rr} in the molecules MO_5 , MO_2L_4 and $\text{MO}_n\text{L}_{4-n}$. For other types of compounds the corresponding equations for the $[G]$ and $[F]$ matrix elements have been derived "per analogiam", taking into account their similar symmetries and arrangement of oxygen atoms with respect to the metal. These matrix elements introduced into the

TABLE XXI

Compound	Symmetry	Species $\nu(\text{MO})$	Activity	Force constant equation	Notes
MO_4	T_d	A_1	Ra	$\lambda = \mu_0(f_r + 3f_{rr})$	[24]
		F_2	IR, Ra	$\lambda = \left[\frac{4}{3} \mu_M + \mu_0 \right] (f_r - f_{rr})$	
LMO_3	C_{3v}	A_1	IR, Ra	$\lambda = [\mu_0 + \mu_M(1 + 2 \cos \alpha)](f_r + 2f_{rr})$	[96]
		E	IR, Ra	$\lambda = [\mu_0 + \mu_M(1 - \cos \alpha)](f_r - f_{rr})$	
L_2MO_2	C_{2v}	A_1	IR, Ra	$\lambda = [\mu_0 + \mu_M(1 + \cos \alpha)](f_r + f_{rr})$	[97]
		B_2	IR, Ra	$\lambda = [\mu_0 + \mu_M(1 - \cos \alpha)](f_r - f_{rr})$	
L_3MO	C_{3v}	A_1	IR, Ra	$\lambda = (\mu_0 + \mu_M)f_r$	[98, 99]
MOL_5	C_{4v}	A_1	IR, Ra	$\lambda = (\mu_0 + \mu_M)f_r$	[67]
Cis- MO_2L_4	C_{2v}	A_1	IR, Ra	$\lambda = (\mu_0 + \mu_M)(f_r + f_{rr})$	[97]
		B_2	IR, Ra	$\lambda = (\mu_0 + \mu_M)(f_r - f_{rr})$	
Trans- MO_2L_4	D_{4h}	A_{1g}	Ra	$\lambda = \mu_0(f_r + f_{rr})$	[97]
		A_{2u}	IR, Ra	$\lambda = (\mu_0 + 2\mu_M)(f_r - f_{rr})$	
Trans-MOXL ₄	C_{4v}	A_1	IR, Ra	$\lambda = (\mu_0 + \mu_M)f_r$	
Cis- MO_3L_3	C_{3v}	A_1	IR, Ra	$\lambda = [\mu_0 + \mu_M(1 + 2 \cos \alpha)](f_r + 2f_{rr})$	
		E	IR, Ra	$\lambda = [\mu_0 + \mu_M(1 - \cos \alpha)](f_r - f_{rr})$	
Trans- MO_3L_3	C_{3v}	A_1	IR, Ra	$\lambda = (\mu_0 + \mu_M)f_r$	
		A_1	IR, Ra	$\lambda = \mu_0(f_r + f_{rr})$	
		B_1	IR, Ra	$\lambda = (\mu_0 + 2\mu_M)(f_r - f_{rr})$	

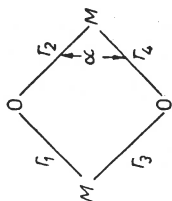
Cis-MOX ₃ L ₂	C _s	A	IR, Ra	$\lambda = (\mu_0 + \mu_M)f_r$
Trans-MOX ₃ L ₂	C _{2v}	A ₁	IR, Ra	$\lambda = (\mu_0 + \mu_M)f_r$
Bent-MOM	C _{2v}	A ₁	IR, Ra	$\lambda = [\mu_M + \mu_0(1 + \cos \alpha)](f_r + f_{rr})$
		B ₂	IR, Ra	$\lambda = [\mu_M + \mu_0(1 - \cos \alpha)](f_r - f_{rr})$
Linear-MOM	D _{∞h}	\sum_g^+	Ra	$\lambda = \mu_M(f_r + f_{rr})$
		\sum_u^+	IR, Ra	$\lambda = (\mu_M + 2\mu_0)(f_r - f_{rr})$
	D _{2h}	A _{1g}	Ra	$\lambda = [\mu_M(1 - \cos \alpha) + \mu_0(1 + \cos \alpha)] \times (f_r + f_{MOM} + f_{OMO})$
		B _{1g}	Ra	$\lambda = [\mu_M(1 + \cos \alpha) + \mu_0(1 - \cos \alpha)] \times (f_r - f_{MOM} - f_{OMO})$
		B _{3u}	IR	$\lambda = (1 + \cos \alpha)(\mu_M + \mu_0)(f_r + f_{MOM} - f_{OMO})$
		B _{2u}	IR	$\lambda = (1 - \cos \alpha)(\mu_M + \mu_0)(f_r - f_{MOM} + f_{OMO})$



Symmetrical coordinates:

$$A_1 : S_1 = \frac{1}{\sqrt{2}} (\Delta r_1 + \Delta r_2)$$

$$B_2 : S_2 = \frac{1}{\sqrt{2}} (\Delta r_1 - \Delta r_2)$$

For (D_{∞h}) $\alpha = 180^\circ$ 

Symmetry coord.:

$$A_{1g} : S_1 = \frac{1}{2} (\Delta r_1 + \Delta r_2 + \Delta r_3 + \Delta r_4)$$

$$B_{1g} : S_2 = \frac{1}{2} (\Delta r_1 - \Delta r_2 - \Delta r_3 - \Delta r_4)$$

$$B_{3u} : S_3 = \frac{1}{2} (\Delta r_1 + \Delta r_2 - \Delta r_3 - \Delta r_4)$$

$$B_{2u} : S_4 = \frac{1}{2} (\Delta r_1 - \Delta r_2 + \Delta r_3 - \Delta r_4)$$

secular equation together with the observed frequencies enabled us to calculate the force constants of the metal-oxygen bonds. The final equations obtained by us are arranged in Table XXI.

The force constants calculated on the basis of the above equation are presented in Tables XXII—XXVI. For the pseudo-tetrahedral anions (Table XXII) the equations derived for T_d symmetry have been employed for calculations, since no X-ray data concerning the angle $\alpha(\text{OMO})$ for all studied compounds are available. μ_0 and μ_M are, as usual, the reciprocal atomic masses of oxygen and metal, respectively, f_r is the stretching force constant, and f_{rr} is the stretch-stretch interaction force constant. The relationship between the observed frequency ν and wavelength λ is:

$$\lambda = 0.588851 \left(\frac{\nu}{1000} \right)^2.$$

The force constants calculated for trioxo-compounds of rhenium and osmium (Table XVI) of symmetry C_{3v} assume the following values:

$$\begin{aligned} \text{Cs}_2[\text{ReO}_3\text{Cl}_3] \quad f_r = 6.96 \quad f_{rr} = 0.31 \\ \text{Cs}[\text{OsO}_3\text{F}_3] \quad f_r = 7.47 \quad f_{rr} = 0.20 \left[\frac{\text{Mdyn}}{\text{\AA}} \right]. \end{aligned}$$

The force constant of a chemical bond is a physical measure of its strength. This value is affected both by the masses of vibrating elements and their mutual affinity. The increase

TABLE XXII

Compound	Symmetry	$\nu_1(A_1)$	$\nu_3(F_2)$	$f_r \left[\frac{-Md}{\text{\AA}} \right]$	$f_{rr} \left[\frac{Md}{\text{\AA}} \right]$	Bond order
ReO_4^-	T_d	986	915	7.52	0.44	} 2.00–2.3
OsO_4	T_d	965	960	8.05	0.24	
RuO_4	T_d	873	920	6.73	0.15	
RuO_4^-	T_d	826	850	5.82	0.20	
RuO_4^{2-}	T_d	857	810	5.56	0.45	

TABLE XXIII

Compound	Symmetry	$\nu(\text{MO})-(A_1)$	$f_r \left[\frac{Md}{\text{\AA}} \right]$	Bond order
$\text{K}_2[\text{ReOCl}_5]$	C_{4v}	993	8.36	} 2.2–2.3
$\text{Cs}_2\text{ReOCl}_5$	C_{4v}	955	7.91	
$\text{Cs}_2\text{ReOCl}_4\text{F}$	C_{4v}	973	8.21	
$[\text{ReO}(\text{OH})\text{en}_2]\text{Cl}_2$	C_{4v}	981	8.35	
$[\text{ReO}(\text{OH})\text{py}_4]\text{Cl}_2$	C_{4v}	965	8.08	
$[\text{ReOCl}_3\text{en}]$	C_s	970	8.16	
$[\text{ReOCl}_3\text{py}_2]$	C_s	971	8.18	
OsOF_5	C_{4v}	960	8.01	

TABLE XXIV

Force constants metal-oxygen bonding in MO₂ systems — symmetry D_{4h}
(Bond order 2)

Compound	$\nu_s(\text{MO}_2)$ A_{1g}	$\nu_{as}(\text{MO}_2)$ A_{2u}	$f_r \left[\frac{Md}{\text{Å}} \right]$	$f_{rr} \left[\frac{Md}{\text{Å}} \right]$
[ReO ₂ en ₂]Cl	890*	819	6.43	1.03
[ReO ₂ py ₄]Cl	890**	822	6.45	1.02
K ₃ [ReO ₂ (CN) ₄]H ₂ O	880*	775	6.06	1.23
[Re ₂ O ₃ en ₂ Cl ₄]	935	800	6.68	1.55
[Re ₂ O ₃ py ₄ Cl ₄]	949	803	6.83	1.65
K ₆ [Re ₂ O ₃ (CN) ₆]	912	784	6.39	1.55
K ₂ [OsO ₂ Cl ₄]	900*	838	6.65	0.98
(NH ₄) ₂ [OsO ₂ Cl ₄]	900**	841	6.67	0.96
Cs ₂ [OsO ₂ Cl ₄]	900**	835	6.63	1.00
K ₂ [OsO ₂ Br ₄]	900**	843	6.68	0.95
(NH ₄) ₂ [OsO ₂ Br ₄]	900**	839	6.65	0.98
K ₂ [OsO ₂ (OH) ₄]	860*	804	6.09	0.87
K ₄ [Os ₂ O ₆ (NO ₂) ₄]	889	843	6.59	0.86
K ₂ [OsO ₂ (NO ₂) ₄]	900**	841	6.67	0.96
K ₂ [OsO ₂ (C ₂ O ₄) ₂]	905**	839	6.69	1.03
Cs[OsO ₂ (C ₂ O ₄) ₂]	905**	834	6.66	1.06
(NH ₄) ₂ [OsO ₂ (C ₂ O ₄) ₂]	905**	837	6.68	1.04
K ₄ [Os ₂ O ₆ (C ₂ O ₄) ₂]	905	820	6.59	1.08
K ₂ [OsO ₂ (CN) ₄]	890*	830	6.51	0.95
Cs[OsO ₂ (CN) ₄]	890**	836	6.55	0.91
Ag ₂ [OsO ₂ (CN) ₄]	890**	832	6.52	0.94
[OsO ₂ (NH ₃) ₄]Cl ₂	870*	828	6.33	0.80
[OsO ₂ (NH ₃) ₄](OH) ₂	870**	831	6.35	0.78
[OsO ₂ (NH ₃) ₄]SO ₄	870**	839	6.41	0.72
Cs ₂ [RuO ₂ Cl ₄]	820**	818	5.56	0.77
Rb ₂ [RuO ₂ Cl ₄]	820**	815	5.54	0.79
Cs ₂ [RuO ₂ Br ₄]	820**	824	5.60	0.74
Y ₂ [RuO ₂ Br ₄]	820**	814	5.54	0.80
Y ₂ [RuO ₂ (SO ₄) ₂]	820**	807	5.50	0.84
[Ru ₂ O ₆ (NH ₃) ₄]	820	795	5.53	0.91

Y = [As(phon)₄]; * value from the Raman spectra of aqueous solutions (Spectrometer IKS-12);
** value assumed for calculations.

in atomic mass of the central metal with respect to the same ligand, *i. e.* oxygen, results in an increase of the force constant. The elements, arranged according to increasing atom mass, form the series Ru < Re < Os. If the metals are arranged according to their affinity to the 2p_π electrons of oxygen, the following sequence will be obtained for a d² electron configuration: Re(V) < Re(VI) < Os(VI). This effect, however, is small in comparison to the metal mass change effect, because the atomic mass of ruthenium is about twice as small as that

Force constants MOM systems — symmetry $D_{\infty h}$

Compound	$\nu_s(\text{MOM})$ Σ_g^+	$\nu_{as}(\text{MOM})$ Σ_u^+	$f_r \left[\frac{\text{Md}}{\text{\AA}} \right]$	$f_{rr} \left[\frac{\text{Md}}{\text{\AA}} \right]$	Bond order
$\text{K}_4[\text{Re}_2\text{OCl}_{10}]$	200	855	3.84	0.54	1.5 1.2
$\text{Cs}_4[\text{Re}_2\text{OCl}_{10}]$	200	851	3.87	0.60	
$[\text{Re}_2\text{O}_3en_2\text{Cl}_4]$	200*	730	3.40	0.99	
$[\text{Re}_2\text{O}_3py_4\text{Cl}_4]$	200*	700	3.30	1.08	
$\text{K}_6[\text{Re}_2\text{O}_3(\text{CN})_8]$	200	752	3.47	0.82	
$(\text{NH}_4)_4[\text{Os}_2\text{OCl}_{10}]$	205*	845	3.97	0.74	
$\text{Y}_4[\text{Os}_2\text{OCl}_{10}]$	205*	838	3.94	0.76	
$\text{Cs}_4[\text{Os}_2\text{OBr}_{10}]$	205*	843	3.96	0.74	
$\text{Y}_4[\text{Os}_2\text{OBr}_{10}]$	205*	845	3.97	0.74	
$\text{Cs}_4[\text{Os}_2\text{OI}_{10}]$	205*	835	3.92	0.78	
$\text{Y}_4[\text{Os}_2\text{OI}_{10}]$	205*	841	3.95	0.75	
$\text{Cs}_4[\text{Os}_2\text{OCl}_6\text{Br}_4]$	205	848	3.98	0.72	
$\text{Y}_4[\text{Os}_2\text{OCl}_6\text{Br}_4]$	204	846	3.94	0.72	
$\text{Cs}_4[\text{Os}_2\text{OClI}_{82}]$	215	832	4.15	1.02	
$\text{Y}_4[\text{Os}_2\text{OClI}_{82}]$	213	830	4.09	0.99	
$\text{K}_4[\text{Ru}_2\text{OCl}_{10}]$	230**	885	3.57	0.14	
$\text{Y}_4[\text{Ru}_2\text{OCl}_{10}]$	230**	880	3.55	0.16	
$\text{K}_4[\text{Ru}_2\text{OBr}_{10}]$	230*	858	3.46	0.26	
$\text{Y}_4[\text{Ru}_2\text{OBr}_{10}]$	230*	861	3.47	0.25	
$\text{Y}_4[\text{Ru}_2\text{OCl}_6\text{Br}_2]$	245	852	3.37	0.20	

* value assumed for calculations

Y — $[\text{As}(\text{phen}_4)]$ ** calculated from overtone $2 \times \nu_s(\text{RuORu})$

TABLE XXVI

Compounds	$\nu(M-\text{OH})$	$f_r \left[\frac{\text{Md}}{\text{\AA}} \right]$
$[\text{Re}(\text{OH})_2en_2]\text{Cl}_3$	571	2.99
$[\text{Re}(\text{OH})_2en_2]\text{F}_3$	554	2.82
$[\text{ReO}(\text{OH})en_2]\text{Cl}_2$	565	2.93
$\text{K}_4[\text{OsO}_2(\text{OH})_4]$	448	1.84
$[\text{Ru}(\text{OH})(\text{NH}_3)_4(\text{NO})]\text{Cl}_2$	574	2.82
$[\text{Ru}(\text{OH})(\text{NH}_3)_4(\text{NO})]\text{Br}_2$	581	2.89
$\text{Ag}_2[\text{Ru}(\text{OH})\text{Cl}_4(\text{NO})]$	528	2.39
$\text{K}_4[\text{Ru}(\text{OH})(\text{NO}_2)_4(\text{NO})]$	584	2.92

of two other elements. For a series of dioxy-compounds one should then expect the following sequence of stretching force constants:

$$f_r[\text{Os}^{\text{VI}}] \approx f_r[\text{Re}^{\text{V}}] > f_r[\text{Ru}^{\text{VI}}].$$

This sequence agrees with experiments (Table XXIV).

The metal-oxygen bonds in mono-oxy compounds of osmium and rhenium (like in trioxy compounds) exhibit comparable values of force constants f_r , what is due to the approximately equal atomic masses of these elements.

A comparison of stretching force constants within the same metal depending on the electron configuration will be interesting. The force field around the central metal increases with the increase in oxidation state. This leads to the force constant increase with the increasing oxidation state and with the increase in the metal-oxygen bond order: $f_r[\text{MOL}_5] > f_r[\text{MO}_2\text{L}_4] > f_r[\text{MOM}] > f_r[\text{M}-\text{OH}]$. A similar series is formed by the force constants f_r of tetrahedral ruthenium anions (Table XXII) namely:



To sum up, it should be emphasized that the calculated values of force constants enabled us to draw certain conclusions regarding the nature and order of the metal-oxygen bonding in complex compounds. On the other hand, thanks to group theory, it was possible to determine the structure and symmetry of the compound studied.

Further support of all conclusions presented in this work is provided by the results of magnetic and spectroscopic studies in the visible and ultraviolet regions [100].

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