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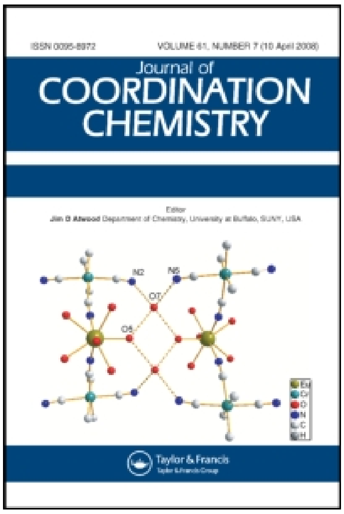

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VIBRATIONAL STUDIES OF DINUCLEAR COMPOUNDS CONTAINING QUADRUPLY BONDED PAIRS OF MOLYBDENUM AND RHENIUM ATOMS

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VIBRATIONAL STUDIES OF DINUCLEAR COMPOUNDS CONTAINING QUADRUPLY BONDED PAIRS OF MOLYBDENUM AND RHENIUM ATOMS[1]

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Infrared and Raman spectra have been recorded for the following dinuclear ions and molecules containing quadruple metal-to-metal bonds: $Re_2Cl_8^{2-}$, $Re_2Br_8^{2-}$, $Mo_2Cl_8^{4-}$, $Re_2(O_2CCH_3)_4Cl_2$, $Re_2(O_2CCH_3)_4Br_2$ and $Mo_2(O_2CCH_3)_4$. The Raman data are, regrettably, rather incomplete due to the intense and extensive electronic absorption spectra of most of the compounds. Intense Raman lines observed at 275 and 289 cm^{-1} for the rhenium compounds and at 406 cm^{-1} for $Mo_2(O_2CCH_3)_4$ have been assigned as predominantly M-M stretching modes. Vibrational analyses using both valence force fields with a few interaction constants and Urey-Bradley force fields lead to moderately consistent results, with the M-M force constants lying in the range 3.1–4.5 mdyne/Å.

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INTRODUCTION

The study of metal-to-metal bonding by means of vibrational spectroscopy has been limited to only about a score of compounds. With the exception of the Hg-Hg stretching frequency reported in 1934 by L. A. Woodward,[3] all of this work has been done within the past decade, and much of it within the last five years. There are several reasons for the apparent neglect of this potentially interesting field: the number of metal-metal bonded compounds known has been limited until very recently; vibrations involving these bonds occur at low frequencies; the vibrations are often forbidden under infrared selection rules and are weak at best when allowed; the compounds are usually too strongly colored for observation of the Raman spectrum with the conventional mercury arc source.

Within the past few years, however, more compounds have been discovered, far infrared equipment has improved, and most important, powerful optical lasers have become available for excitation of the Raman spectra of many strongly colored materials. The variety of compounds studied is still somewhat limited, but metal-to-metal stretching frequencies have been observed for polynuclear metal carbonyls;[4–8] mercurous halides;[3,7,9] lead, bismuth and thallium hydroxides and alkoxides;[10] and several metal alkyls.[7,11] The subject has recently been reviewed.[12]

In the above compounds, which have relatively low metal-to-metal bond orders, the metal-metal stretching frequency has usually been observed in the Raman spectrum between 100 and 200 cm^{-1}, and normal coordinate calculations yield force constants in the range 1–2 mdyne/Å. In the dinuclear halides and carboxylates of rhenium and molybdenum, the short metal-to-metal distances indicate the presence of strong multiple bonds, and molecular orbital calculations have suggested a bond order of four.[13,14] If the quadruple bond is as strong as the bond lengths indicate, then the metal-metal stretching frequencies should lie considerably higher than any observed for the weaker metal bonds, and vibrational analyses should yield substantially higher force constants. In an attempt to determine both the frequencies and the force constants of quadruple metal-metal bond stretching, a study of the vibrational spectra of the $Re_2Cl_8^{2-}$, $Re_2Br_8^{2-}$ and $Mo_2Cl_8^{4-}$ ions, and the $Re_2(CH_3COO)_4X_2$ ($X = Cl$, Br), and $Mo_2(CH_3COO)_4$ molecules was undertaken.

EXPERIMENTAL

The compounds were all prepared by literature methods. The octachlorodirhenate(III) ion was prepared by the molten salt method[15,16] and precipitated as the *n*-butylammonium salt. The

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pyridinium salt was prepared by precipitation from an acidic methanol solution of the butylammonium salt. The analogous $Re_2Br_8^{2-}$ salts were prepared by halogen exchange with the chloride compounds in aqueous HBr-methanol solutions.[17] The *n*-butylammonium salts of the dimeric rhenium halide anions were used to prepare the acetates, $Re_2(CH_3COO)_4X_2(X = Cl,\ Br)$.[17] Molybdenum acetate, $Mo_2(CH_3COO)_4$, was prepared from the hexacarbonyl by the method of Wilkinson.[18] Several $Mo_2Cl_8^{4-}$ salts[19] were kindly supplied by J. V. Brencic. All the compounds were thoroughly washed with appropriate solvents and dried at room temperature *in vacuo*.

Infrared spectra of the acetates were recorded in the range 1600–250 cm^{-1} on a Perkin–Elmer 521 spectrophotometer using KBr pellets. Spectra were also recorded on Nujol mulls between KBr plates in this region and were identical with the pellet spectra. The range 400–40 cm^{-1} was recorded for all the compounds with a Perkin–Elmer 301 far infrared spectrophotometer in double beam mode, employing Nujol mulls supported on polyethylene plates with a polyethylene-Nujol blank in the reference beam. Peak positions on the Model 521 spectra could be determined to within about 2–3 cm^{-1}, while the data obtained with the Model 301 are probably good to about ±1 cm^{-1}. Raman spectra for all the compounds were recorded on Cary 81 instruments using the 6328 Å line of the He–Ne laser to excite the spectra of the acetates and the bromide and the 4765 Å line of the argon ion laser for the blue chlorides.

RESULTS

$Re_2Cl_8^{2-}$ The vibrational spectra of the solid butylammonium and pyridinium salts of this ion are shown in Figure 1. The Raman spectra are complicated by the presence of unfiltered lamp lines in the spectrum of the argon ion laser which obscure the regions where metal chlorine stretching and bending are expected. However, a very intense line was detected for each compound at about

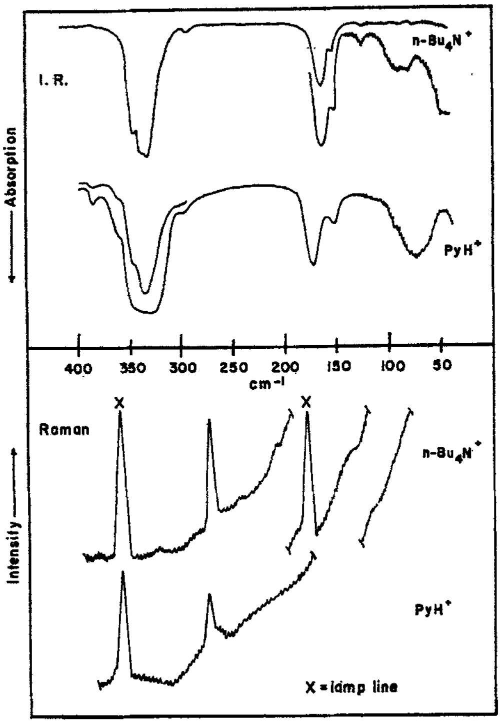

FIGURE 1. Infrared and Raman spectra of butylammonium and pyridinium salts of $Re_2Cl_8^{2-}$. Infrared spectra recorded on Nujol mulls. Raman spectra recorded on solid samples using 4765 Å line of argon ion laser.

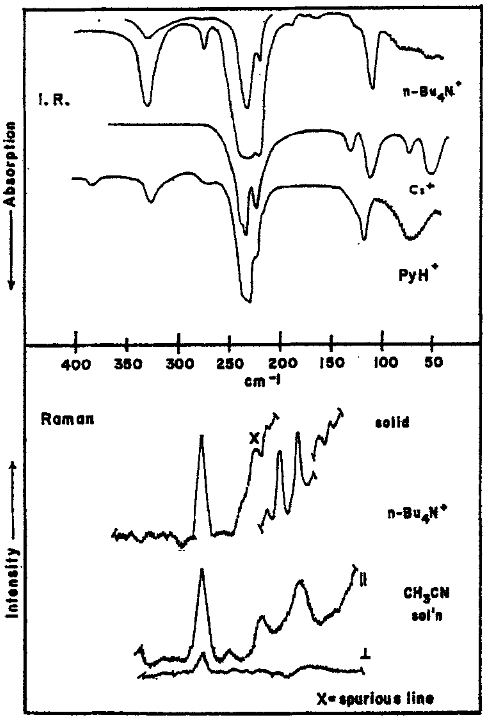

FIGURE 2. Infrared spectrun of $Cs_2Re_2Br_8$. Infrared and Raman spectra of butylammonium and pyridinium salts of $Re_2Br_8^{2-}$. Infrared spectra recorded on Nujol mulls. Raman spectra on solid and CH_3CN solution using 6328 Å line of He—Ne laser.

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TABLE I

Observed frequencies of $Re_2X_8{}^{2-}$ salts (cm^{-1})[a]

Infrared

$Re_2Cl_8{}^{2-}$		$Re_2Br_8{}^{2-}$		
Bu_4N^+	PyH^+	Bu_4N^+	PyH^+	Cs^+
—	386 vw	—	386 vw	—
—	360 vw(sh)	330 w	327 w	—
347 s	347 s(sh)	275 vw	273 vw	237 (sh)
338 s		232 s	233 s	233 s
334 s	334 s(br)	220 m	223 m(sh)	221 m
295 vw	300 vw	—	213 vw(sh)	—
163 m	173 m	124 w(sh)	[b]	130 vwk
154 m	153 m	109 m	117 m(br)	118 m
124 vw	120 vw(sh)?	78 vw	71 m(br)	68 wk
88 w	77 m(br)	54 vw		56 m
~ 50 m				

Raman

		Bu_4N^+		
Bu_4N^+	PyH^+	Solid	CH_3CN solution	Cs^+ Solid
294 w(sh)		277 vs	277 vs(P)[c]	275 m
273 vs	275 vs	213 w	250 m	
244 vw		200 m	216 m	
210 w		184 m	183 s(P)[c]	
140 w(sh)?		164 w		
115 w(sh)?		152 w		

[a] Qualitative intensities: s, strong; m, medium; w, weak; (sh), shoulder; (br), broad; ?, existence of the peak is questionable. (P) indicates that the Raman band was observed to be polarized.

[b] Broad unresolved shoulder on following peak at 117 cm^{-1} corresponding to this frequency.

[c] While the results in Figure 2 would permit the conclusion that all four bands are polarized, the effect is indistinct for the two weaker bands. For the stronger bands, at 277 and 183 cm^{-1} the result is very pronounced. Since only two A_{1g} bands can be expected in this spectral region, it seemed reasonable to assign the polarizations as we have done.

275 cm^{-1}. The same peak was observed using a helium-neon laser, but absorption of this red exciting source by the bright blue chloride salts prevented its further use. Table I presents numerical frequency data for these spectra.

$Re_2Br_8{}^{2-}$ Infrared spectra recorded from solid samples of the butylammonium, pyridinium and cesium salts of $Re_2Br_8{}^{2-}$ are given in Figure 2, along with Raman spectra of a solid sample and a CH_3CN solution of the butylammonium salt, obtained with a helium-neon laser. Numerical data from these spectra are also contained in Table I.

$Mo_2Cl_8{}^{4-}$ Infrared spectra of both $K_4Mo_2Cl_8$ and $K_4Mo_2Cl_8 \cdot 2H_2O$ are shown in Figure 3. Numerical data from these spectra and the Raman spectra, recorded with the helium-neon laser, are given in Table II. Only one Raman band was observed for each salt at about 260 cm^{-1}. The $Mo_2Cl_8{}^{4-}$ ion strongly absorbs the lines of the argon ion laser and no attempt has been made to record its Raman spectrum using this source.

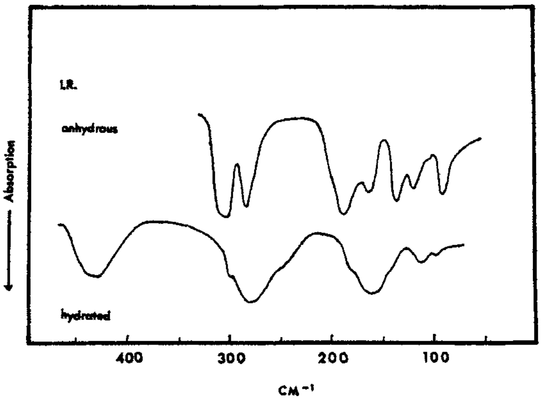

FIGURE 3. Infrared spectra of $K_4Mo_2Cl_8$ and $K_4Mo_2Cl_8 \cdot 2H_2O$, recorded on mineral oil mull specimens.

Acetates Complete infrared and Raman spectra for solid samples of molybdenum acetate and rhenium acetate chloride are shown in Figure 4 with significant details of the rhenium bromide analogue included where they differ from the chloride. Tables III and IV give the numerical frequencies observed for the molybdenum and rhenium compounds respectively. The Raman spectra were all recorded with the helium-neon laser source.

TABLE II

Observed frequencies of $Mo_2Cl_8{}^{4-}$ salts (cm $^{-1}$)[a]

$K_4Mo_2Cl_8$	$K_4Mo_2Cl_8.2H_2O$
Infrared	
	(3535) m
	(3485) m
	(1640) w
	434 s
302 s	300(sh)
275 s	288 s
—	243 (sh)
183 m	188 (sh)
160 m	160 m
128 s	142 vw
113 m	115 w
102 vw	108 vw
91 m	91 vw?
Raman	
~260	~260

[a] Frequencies in parentheses correspond to the internal motions of the water molecules. Qualitative intensities: s, strong; m, medium; w, weak; (sh), shoulder; ?, existence of the peak is questionable.

TABLE III

Observed frequencies of $Mo_2(O_2CCH_3)(Cm^{-1})_4$[a]

Infrared	Raman
1510 s	1450 m
1492 m	1432 s
1440 s	1365 w
1410 m	1360 w
1352 m	1055 w
1045 m	950 s
1030 m	690 s
937 m	686 s
675 s	635 vw
630 m	567 vw
570 w	488 vw
369 s	406 vs
348 s	322 w
338 s	315 vw
228 m	299 w
175 w	215 vw?
143 w	200 m
92 w	187 m
55 vw	100 vw?
46 vw	

[a] Qualitative intensities: s, strong; m, medium; w, weak; v, very; ?, questionable peak.

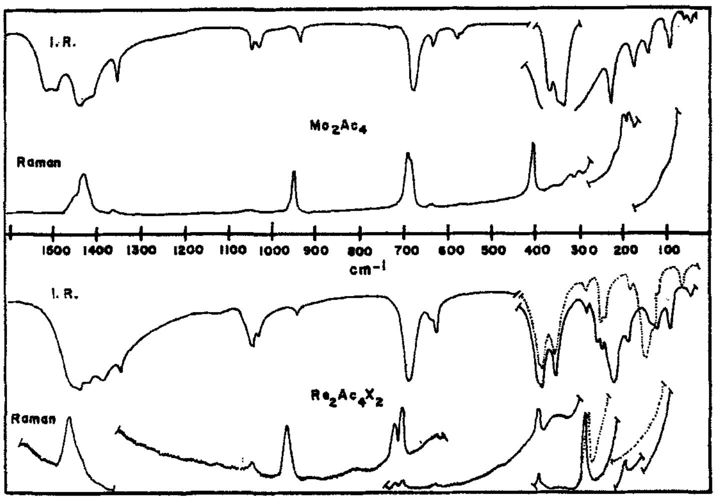

FIGURE 4. Infrared and Raman spectra of rhenium and molybdenum acetates. Infrared spectra recorded on KBr pellets and Nujol mulls. Raman spectra recorded on solid samples using 6328 A line of He—Ne laser. Solid trace in $Re_2Ac_4X_2$ spectra is for X=Cl; broken trace is for X=Br.

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TABLE IV

Observed frequencies of $Re_2(O_2CCH_3)_4X_2$ (cm^{-1})[a]

Infrared		Raman	
Cl	*Br*	*Cl*	*Br*
1450 s(br)	1450 s(br)	1466 s	—
1385 s	1382 s	1400 m(sh)	—
1345 w	1345 w	1052 vw	—
1047 m	1044 w	965 s	963 s
1023 w	1025 w	918 vw	—
952 w	949 w	721 s	720 s
685 s	683 s	704 s	703 s
640 w	638 w	625 vw	—
629 m	627 m	420vw(sh)?	—
396 s	395 s	397 s	392 s
390 s	389 s	289 vs	280 vs
356 s	355 s	199 s	
286 vw	285 vw		
262 m	262 m		
251 m	254 m		
223 s	—		
188 m	187 m		
—	150 s		
135 m	135 w(sh)		
123 m	124 w(sh)		
93 m	—		
—	65 m		
45 w			

[a] Qualitative intensities: s, strong; m, medium; w, weak; v, very; (sh), shoulder; ?, questionable peak.

ASSIGNMENTS AND NORMAL COORDINATE CALCULATIONS

For an M_2X_8 skeleton with D_{4h} symmetry, as shown in Figure 5, there should be five infrared active vibrations and nine Raman active vibrations, as shown in detail in Table V. The ir modes include two M–X stretches (A_{2u}, E_u) and three angle deformations ($2E_u$, A_{2u}), while the Raman bands include the M–M stretch (A_{1g}), three M—X stretches (A_{1g}, B_{1g}, E_g) and five bending modes (A_{1g}, B_{1g}, $2E_g$).

$Re_2X_8^{2-}$ As shown in Figure 1 and Table I, there are two bands in the spectra of the $Re_2Cl_8^{2-}$ salts (a doublet at ~335 cm^{-1} and one at 347 cm^{-1}) of appropriate frequencies to be the Re—Cl stretching modes. They are so similar in frequency that the correctness of the symmetry assignments is not a crucial matter in the relatively crude normal coordinate calculations we have been able to perform. Tentatively we have assigned the doublet centered at ~335 cm^{-1} to the E_u mode and the band at 347 cm^{-1} to the A_{2u} mode.

At lower frequencies the three bending modes are observable at 163, 154 and 124 cm^{-1} in the butylammonium salt, while only two are clearly resolved in the pyridinium compound at 173 and 153 cm^{-1}. The third bending mode may be the very weak, indistinct shoulder at about 120 cm^{-1} in this compound. The most intense peak with the highest frequency for both compounds is assigned to the A_{2u} vibration, because this mode involves the out-of-phase umbrella motions of both ends of the molecule, and is likely to be the most intense of the bending modes. The next most intense peak should probably correspond to the E_u mode involving X–M–X bending, and the third and weakest peak must then be assigned to the E_u M–M–X bending mode.

The low frequency peaks in both compounds

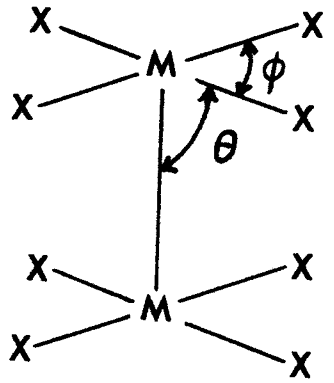

FIGURE 5. The M_2X_8 skeleton (D_{4h} symmetry) with the bond angles θ and ϕ defined.

TABLE V

Symmetry of normal modes and internal coordinates for M_2X_8 species[a]

	(Point Group D_{4h})								
	$\underline{\underline{A_{1g}}}$	$\underline{\underline{B_{1g}}}$	$\underline{\underline{B_{2g}}}$	$\underline{\underline{E_g}}$	A_{1u}	$\underline{A_{2u}}$	B_{1u}	B_{2u}	$\underline{E_u}$
24 Normal modes	3	2	1	3	1	2	1	2	3
1 M–M (R)	1								
8 M–X (r)	1	1		1		1		1	1
8 M–M–X (θ)	1[b]	1		1		1[b]		1	1
8 M–M–X (ϕ)	1[b]		1	1		1[b]	1		1
1 M–M torsion					1				

[a] Single underlined symmetry species are infrared active; double underlined species are Raman active.

[b] Symmetry species A_{1g} and A_{2u} contain one redundancy each in the angle bending coordinates θ and ϕ.

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are probably lattice modes, but the origin of the weak absorption close to 300 cm^{-1} as well as the shoulder at 360 cm^{-1} in the pyridinium salt is obscure. These may be due to activation of an unallowed vibration, or to some combination or overtone band. The weak peak at 386 cm^{-1} in the pyridinium salt is presumably due to vibration of the cation, since the same peak is observed in the $Re_2Br_8^{2-}$ salt.

The Raman spectra shown in Figure 1 are disappointing because of the lamp lines which obscure the M—X stretching and bending regions. The very intense peak observed at about 275 cm^{-1} in both compounds can be assigned to the M—M stretching frequency, but the nature and even the existence of the other weak peaks is uncertain.

The infrared spectra (Figure 2 and Table I) for $Re_2Br_8^{2-}$ have the same general appearance as those obtained for the chlorides. Frequency shifts of the stretching and bending modes are what would be expected from mass differences of the halogen atoms. The order of intensity differs, however, in both regions from that observed for $Re_2Cl_8^{2-}$; the higher frequency stretching modes being more intense while just the opposite holds for the bends. In making assignments, the relative intensities of the peaks were judged to be more significant than the relative frequencies, so that the more intense stretching mode at 233 cm^{-1} was assigned to the E_u mode, and the weaker peak at 220 cm^{-1} was assumed to be the antisymmetric breathing mode of symmetry A_{2u}. The existence of a shoulder on the side of the 233 cm^{-1} band in the cesium compound supports this assignment. Again, however, the normal coordinate calculations are of such an approximate nature that the correctness of this assignment is not crucial.

In the bending region, the three expected peaks are observed for the butylammonium and the cesium salts, but only two peaks are seen for the pyridinium compound. The bands were assigned on the basis of their intensities as 124, 109 and 78 cm^{-1} for the E_u, A_{2u} and E_u modes, respectively, of the butylammonium salt, 117 and 71 cm^{-1} for the A_{2u} and E_u vibrations, respectively, of the pyridinium compound and 130, 118 and 68 cm^{-1} for the E_u, A_{2u} and E_u modes, respectively, of the cesium salt.

The low energy bands observed for the butylammonium and cesium compounds are presumed to be lattice modes. The weak peak near 330 cm^{-1} is probably due to chloride impurity, and the very weak feature at about 275 cm^{-1} may be the forbidden M—M stretch. The weak peak at 386 cm^{-1} is probably due to the pyridinium cation. Other weak features are unexplained.

The solid and solution Raman spectra of the butylammonium salt are much better than the corresponding results for the chloride. The four peaks observed in the solution spectrum may be assigned to the M—M and M—X stretching modes, with the polarization data unequivocally identifying the A_{1g} M—M and M—X stretches as those at 277 and 183 cm^{-1} respectively. The next most intense peak at 216 cm^{-1} was assigned to the B_{1g} M—X mode, leaving the peak at 250 cm^{-1} as the E_g M—X stretch. The weak features at 164 and 152 cm^{-1} are presumably due to bending modes; their assignment is uncertain, though the former is probably the B_{2g} mode and the latter, one of the E_g modes.

Using the assignments just described normal coordinate calculations were carried out for the $Re_2X_8^{2-}$ ions. The G matrices were computed using GMAT,[20a] a computer program written by J. H. Schachtschneider of Shell Development Co., and molecular dimensions were taken from published crystal structure determinations.[21, 22] The calculations were carried out using Schachtschneider's program FPERT[20b] for iterative fitting of calculated to observed frequencies.

For the $Re_2Br_8^{2-}$ ion calculations were made using both a valence force field and a Urey–Bradley force field. In the first case, the diagonal constants F_{ReRe}, F_{ReBr}, F_θ and F_ϕ (see Figure 5) as well as the ReBr . . . ReBr interaction constants F_{rr} (*cis*) and F_{rr} (*trans*) were used to fit eight observed frequencies. In the Urey–Bradley force field the same six force constants plus another one, F_{rr}'' pertaining to the interaction between stretching of nearest ReBr bonds on opposite ends of the molecule were used to fit nine frequencies. The results of these calculations are shown in Table VI. The general agreement between observed and calculated frequencies tends to confirm the assignments. It is notable, however, that the Urey–Bradley field gives a distinctly poorer fit. The potential energy distributions among the internal coordinates are also summarized. The force constants themselves are given in Table VII. It appears that the valence force field, in which the nonbonded interactions must be accounted for entirely by the valence force constants, and particularly by the interaction constants is not entirely satisfactory, since the values of F_{rr} and F_{rr}' seem rather unrealistic. On the other hand, the Urey–Bradley force field

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gives what would seem to be unrealistically small values of F_θ and F_ϕ. While the two treatments give essentially identical values for F_{ReCl} which are very reasonable, they give somewhat different values for F_{ReRe}, *viz.* 3.13 and 3.37 md/A. However, the difference is not alarming and presumably some physical significance can be attached to their mean of ~3.2 md/A.

For the $Re_2Cl_8{}^{2-}$ ion, where the data were considerably less complete (only one Raman line) only a valance force field calculation was carried out. The results, summarized in Table VIII, were obtained by fitting four diagonal force constants to six observed frequencies, with F_{rr} and F_{rr}' being transferred from the $Re_2Br_8{}^{2-}$ calculation.

$Mo_2Cl_8{}^{4-}$ The differences which can be observed between the infrared spectra of the two potassium salts arise from the presence of water molecules in one of them. Beyond the three high energy bands due to the stretching and bending modes of these molecules, a strong broad band appears at 434 cm^{-1}

TABLE VI

Observed and calculated normal vibrations for $Re_2Br_8{}^{2-}$ frequencies (cm^{-1})

Symmetry		Observed	Valence Force Field	Urey–Bradley Force Field	Assignment and PE Distribution[a]
A_{1g}	1	277	276	278	MM(64), MX(22)
	2	184	189	174	MX(63), MM(22)
	3	—	65	65	MMX(57), XMX(27), MM(14)
B_{1g}	4	216	216	182	MX(75)
	5	—	57	59	MMX(100)
B_{2g}	6	—	152	146	XMX(100)
E_g	7	250	252	274	MX(88), MMX(21)
	8	—	127	127	XMX(66), MX(36)
	9	—	95	95	MMX(72), XMX(21)
A_{1u}	10	—	—	—	M-M-Torsion
A_{2u}	11	220	218	194	MX(82)
	12	112	107	107	MMX(65), XMX(32)
B_{1u}	13	—	152	146	XMX(100)
B_{2u}	14	—	216	182	MX(75)
	15	—	57	59	MMX(100)
E_u	16	233	230	254	MX(85), XMX(15)
	17	127	124	121	XMX(80), MX(20)
	18	(73)[b]	57	59	MMX(99)

[a] Based on Valence Force Field. Percent contributions of internal coordinates to normal coordinate in parentheses; total need not be 100 because only contributions > 10% are noted.
[b] Not used in refining Valence Force Field.

TABLE VII

Calculated force constants (in md/A)

Molecule	Force Field	F_{MM}	F_{MX}	F_{MO}	F_θ	F_ϕ	F_{rr}	F_{rr}'	F_{rr}''
$Re_2Br_8{}^{2-}$	valence	3.13	1.65	—	0.94	1.80	−0.06	0.42	—
$Re_2Br_8{}^{2-}$	Urey–Bradley	3.37	1.62	—	0.4	0.1	0.44	−0.29	0.14
$Re_2Cl_8{}^{2-}$	valence	3.77	2.10	—	1.62	1.03	−0.06[a]	0.42[a]	—
$Mo_2(O_2CCH_3)_4$	Urey–Bradley	3.76	—	1.08	−0.22	0.1	0.11	−0.05	0.3
$Re_2(O_2CCH_3)_4Cl_2$	valence	4.47	0.87	—[b]	—[b]	—[b]	—[b]	—[b]	—[b]

[a] Values for F_{rr} and F_{rr}' were transferred from the bromide dimer and not refined.
[b] Not calculated, see text.

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in the hydrated salt only. The bands are generally much broader in the hydrated salt and a few of them are observed only as shoulders on the side of strong bands whereas the bands are generally well separated in the anhydrous compound. Thus in the hydrate the 300 cm^{-1} band is a shoulder on the 288 cm^{-1} band and the 188 cm^{-1} band a shoulder on the side of the very broad 160 cm^{-1} band.

In $K_4Mo_2Cl_8$, two strong bands are observed in the stretching region. On the basis of their intensities and widths, the 302 cm^{-1} band is assigned to the E_u mode and the 275 cm^{-1} band to the A_{2u} mode. Among the lower frequencies, 183, 160 and 128 cm^{-1} are probably the three expected bending modes and are assigned to the E_u, A_{2u} and E_u vibrations, respectively, by comparison with the corresponding frequencies of the rhenium compounds.

In the hydrated compound the two stretching modes are at 300 cm^{-1} and 288 cm^{-1} and the three bending modes at 188 cm^{-1} (E_u), 160 cm^{-1} (A_{2u}) and 142 cm^{-1} (E_u).

The weak feature at 243 cm^{-1} remains unexplained. In both salts, the lower energy bands are probably lattice modes.

No force constants were calculated for $Mo_2Cl_8^{4-}$. Since Raman data are entirely unavailable, no useful information on F_{MoMo} could be obtained.

Dimolybdenum Tetraacetate This molecule was treated in a restricted way. Because, on the one hand, the higher frequencies due to modes localized in the acetato groups are of no interest in the present context, while, on the other hand, there are great difficulties and ambiguities involved in assigning the modes in the $\overline{\mathrm{MoMoOCO}}$ rings, only the Mo_2O_8 skeleton was explicitly treated. Attempts were actually made to include the rings in the calculations but these calculations could not be made to converge satisfactorily. The results obtained did suggest, however, that omitting the rings will lead to values of the M—M stretching constant which are roughly 10% too high.

The strong Raman line at 406 cm^{-1} was assumed to be unambiguously assignable to the A_{1g} mode consisting primarily of Mo—Mo stretching. The infrared bands at 343 (actually a doublet, 338, 348) and 369 cm^{-1} were taken to be Mo—O stretches and the infrared bands at 143, 175 and 228 cm^{-1} were assumed to be skeletal bending modes. The explicit assignment of these five infrared bands to

TABLE VIII

Observed and calculated normal vibrations for $Re_2Cl_8^{2-}$[a]

Symmetry		Frequencies (cm^{-1}) Observed	Calculated	Assignment[b]
A_{1g}	1	—	359	MX(73), MM(13)
	2	274	274	MM(65), MX(14), MMX(17)
	3	(115)	117	MMX(69), MM(22)
B_{1g}	4	—	356	MX(80)
	5	(115)	122	MMX(100)
B_{2g}	6	—	189	XMX(100)
E_g	7	—	351	MX(85), MMX(13)
	8	—	185	MMX(75), MX(15), XMX(10)
	9	(140)	145	XMX(87),MMX(13)
A_{1u}	10	—	—	MM Torsion
A_{2u}	11	347	347	MX(87)
	12	164	168	MMX(88), XMX(12)
B_{1u}	13	—	189	XMX(100)
B_{2u}	14	—	356	MX(80)
	15	—	122	MMX(100)
E_u	16	335	334	MX(98)
	17	154	155	XMX(89), MMX(10)
	18	124	119	MMX(90)

[a] Observed frequencies in parentheses not included in refinement due to questionably validity.

[b] Assignments based on potential energy distribution, arranged in decreasing order of importance; percent contributions from Δ(Re-Re), Δ(Re-Cl), Δθ and Δϕ are given in parentheses. These precentages may total less than 100 because contributions < 10% are omitted.

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the A_{2u} and E_u symmetry species remained unsettled. For the stretching modes, it appeared that the doublet at 338, 348 cm^{-1} might plausibly be assigned as the E_u mode slightly split by low symmetry in the crystal environment; the band at 369 cm^{-1} would then have to be due to the A_{2u} mode. However, this assignment proved unsatisfactory as shown in Table IX. It may be seen from calculations (1) and (2) that regardless of how the bending modes are assigned a reversal in the assignment of the stretching frequencies (i.e., so as to have $\nu(E_u) > \nu(A_{2u})$) is clearly demanded. Moreover, it also appears from calculations (1) and (2) that for the bending modes the preferred order should be $\nu(A_{2u}) > \nu(E_u)$.

TABLE IX

Results of alternate assignments for Mo_2O_8 skeleton

		Calculation Number							
		(1)		(2)		(3)		(4)	
Symmetry species	Mode Number	Assignment	Calc'd freqs.	Assignment	Calc'd freqs.	Assignment	Calc'd freqs.	Assignment	Calc'd freqs.
A_{1g}	1	406	406	406	406	406	406	406	406
	2		321		321		328		324
	3		147		162		162		152
B_{1g}	4		321		321		328		324
	5		156		176		176		162
B_{2g}	6		180		180		181	187	184
E_g	7		389		396		403		395
	8		215		238		239	200	224
	9		131		132		133		134
A_{1u}	10		—		—		—		—
A_{2u}	11	369	321	369	321	343	328	338	325
	12	175	201	228	227	228	227	228	210
B_{1u}	13		180		180		181		184
B_{2u}	14		321		321		328		325
	15		156		176		176		163
E_u	16	343	373	343	373	369	381	369	377
	17	228	156	175	176	175	175	175	163
	18	143	142	143	142	143	143	143	144
Calculated K_{MoMo}, md/A		3.89		3.65		3.65		3.76	
Av. error of Fit, cm^{-1}		30		13		5		10	

On the basis of these results, calculation (3) was carried out; the assigned and calculated frequencies now agree rather well (average discrepancy of only 5 cm^{-1}). On the assumption that assignment (3) is correct as far as it goes, it was then extended slightly by adding two more assigned frequencies in order to make calculation (4) in which bending constants were also explicitly included. The agreement between assigned and calculated frequencies is still satisfactory. The force constants obtained from calculation (4) are recorded in Table VII.

It is interesting to note that the Mo—Mo stretching force constant is relatively insensitive to the assignment of the Mo—O stretching and angle bending frequencies; indeed as comparison of calculations (2) and (3) shows, K_{MoMo}, is *entirely* insensitive to the assignment of the Mo—O stretching modes. This is because the F matrix contains no interaction constant between Mo—Mo and Mo—O stretching motions and the geometry is such that no interaction occurs *via* the G matrix (because the two types of internal coordinate are almost precisely orthogonal). In fact, a calculation of the potential energy distribution for ν_1 shows that it consists of about 75% Mo—Mo stretching and 25% θ angle bending, with no significant contribution from Mo—O stretching.

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$Re_2(O_2CCH_3)_4X_2$ For these molecules there will be symmetric (A_{1g}) and antisymmetric (A_{2u}) Re—X stretching modes as well as symmetric (E_g) and antisymmetric (E_u) X wagging modes in addition to the set of normal modes inherent in the $M_2(O_2CCH_3)_4$ portion of the molecule. In the case of $Mo_2(O_2CCH_3)_4$ it was shown that the calculated value of the Mo—Mo force constant was relatively insensitive to the frequencies assigned to the bending modes and almost entirely insensitive to the values of the metal-oxygen stretching modes. For the compound $Re_2(O_2CCH_3)_4Cl_2$, therefore, it was felt that a satisfactory approximate calculation of K_{ReRe} could be made by treating only the heavy atom skeleton, Cl—Re—Re—Cl. Indeed, only the two A_{1g} and the A_{2u} vibrations need to be considered. From the data given in Table IV the following assignments were made:

$$A_{1g}: \begin{cases} \text{Re—Re Stretch, } 289\ \text{cm}^{-1} \\ \text{Re—Cl Stretch, } 199\ \text{cm}^{-1} \end{cases}$$

$$A_{2u}: \quad \text{Re—Cl Stretch, } 223\ \text{cm}^{-1}$$

The assignment of the Re—Cl stretches to such low frequencies, though virtually mandatory from the comparison of the $Re_2(O_2CCH_3)_4Cl_2$ and $Re_2(O_2CCH_3)_4Br_2$ spectra, might seem unlikely since M—Cl stretching modes for heavy metals, M, are generally found[23] in the range 300–400 cm^{-1}. However, the Re—Cl distances[24] in $Re_2(O_2CC_6H_5)_4Cl_2$, 2.49Å, are considerably longer than those normally found in Re^{III} chloro species such as $Re_2Cl_8^{2-}$, $Re_2Cl_6(PR_3)_2$, etc., namely 2.30–2.35 Å. Hence significantly lower Re—Cl stretching frequencies are to be expected.

Using the above assignment and a simple force field consisting of F_{ReRe}, F_{ReCl} and F_{Rr}, a constant pertaining to interaction between the stretches of these two types of bonds, the force constants shown in Table VII were calculated. F_{Rr} had the value 0.22 md/Å.

DISCUSSION

The purpose of this study, as it was finally executed and reported here, is to provide a semiquantitative indication of the strength of the quadruple Re—Re and Mo—Mo bonds. Initially more detailed and precise results and conclusions were hoped for, but these hopes were tempered, and finally curtailed, by practical difficulties encountered, especially the limited amount of Raman data obtainable, the lack of criteria for making definitive assignments and computational problems encountered[25] in treating the complex polycyclic acetato bridged species.

While the calculations reported here are sufficiently crude that no close interpretation of the numerical values of the force constants F_{ReRe} and F_{MoMo} would be defensible, and it is possible that individual values could be in error by perhaps as much as ±20%, the general range, 3.0–4.5 md/Å, in which the calculated values are found certainly carries the strong, essentially unequivocal, implication that the Re—Re and Mo—Mo bonds are very strong and hence multiple in nature. Since bond stretching force constants have a roughly linear dependence on bond order, it may be argued that since single bonds between heavy transition metal atoms have force constants[12] of around 1.0 md/Å, the present results suggest that the Re—Re and Mo—Mo bonds studied here have bond orders of 3–4. Thus, strong independent support is provided for the previously proposed formulation[13,14] of these bonds as quadruple ones, consisting of rather strong σ and π (twice) components plus a weaker but well-defined δ component.

It is interesting to note that the Raman lines due to those vibrational modes which are primarily metal-metal stretching motions are exceptionally strong. This is qualitatively in accord with the approximately linear relationship[26] between the order of a bond and its polarizability. It would probably be worthwhile to investigate this relationship more quantitatively for these strong M—M bonds. At present, however, there are no plans for doing so in this laboratory.

REFERENCES

1. Supported in part by the United States Atomic Energy Commission.
2. NATO Fellow on leave from Faculté des Sciences de Paris, France.
3. L. A. Woodward, *Phil. Mag.* **18**, 823 (1934).
4. C. O. Quicksall and T. G. Spiro, *Inorg. Chem.* **7**, 2365 (1969).
5. C. O. Quicksall and T. G. Spiro, *Chem. Comm.* 839 (1967).
6. D. Hartley, P. A. Kilty, and M. J. Ware, *Chem. Comm.* 493 (1968).
7. H. M. Gager, J. Lewis, and M. J. Ware, *Chem. Comm.* 616 (1966).
8. F. A. Cotton and R. M. Wing, *Inorg. Chem.* **4**, 1328 (1965).

9. J. R. Durig, *et al.*, *J. Chem. Phys.* **50**, 2130 (1969).
10. V. A. Maroni and T. G. Spiro, *Inorg. Chem.* **7**, 188, 193 (1968).
11. N. A. D. Carey and H. C. Clark, *Chem. Comm.* 292 (1967).
12. T. G. Spiro, *Progr. Inorg. Chem.* **11**, 1 (1970).
13. F. A. Cotton, *Inorg. Chem.* **4**, 334 (1965).
14. F. A. Cotton and C. B. Harris, *Inorg. Chem.* **6**, 924 (1967).
15. R. A. Bailey and J. A. McIntyre, *Inorg. Chem.* **5**, 1940 (1966).
16. A. B. Brignole and F. A. Cotton, *Inorg. Syn.* **13**. In press.
17. F. A. Cotton, *et al.*, *Inorg. Chem.* **4**, 326 (1965).
18. T. A. Stephenson, E. Bannister, and G. Wilkinson, *J. Chem. Soc.* 2538 (1964).
19. J. V. Brencic and F. A. Cotton, *Inorg. Chem.* **9**, (1970).
20. (a) J. H. Schachtschneider, *Technical Report No.* 231–64 (Shell Development Co., Emeryville, California, 1964). (b) *Technical Report No.* 57–65 (Shell Development Co., Emeryville, California, 1965).
21. F. A. Cotton and C. B. Harris, *Inorg. Chem.* **4**, 330 (1965).
22. F. A. Cotton, B. G. DeBoer, and M. Jeremic, *Inorg. Chem.* **9**, 2143 (1970).
23. D. M. Adams, *Metal-Ligand and Related Vibrations* (Edward Arnold, Ltd., London, 1967).
24. M. J. Bennett, W. K. Bratton, F. A. Cotton and W. R. Robinson, *Inorg. Chem.* **7**, 1570 (1968).
25. W. K. Bratton, Ph.D. Thesis, M.I.T., 1969.
26. T. V. Long and R. A. Plane, *J. Chem. Phys.* **43**, 475 (1965).

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