five carbon atoms being only 0.018 Å. The perpendicular distance to this least-squares plane from the iridium atom is 1.936 Å.

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Supplementary Material Available. A listing of structure factor amplitudes (Table V) will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th Street, N.W., Washington, D.C. 20036. Remit check or money order for $4.50 for photocopy or $2.50 for microfiche, referring to code number JACS-75-2686.

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Resonance Raman and Electronic Spectra of Various Salts of the $Mo_2Cl_8{}^{4-}$ Ion[1]

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Abstract: Rigorous resonance Raman spectra of the complexes $(enH_2)_2Mo_2Cl_8{\cdot}2H_2O$, $K_4Mo_2Cl_8$, $Cs_4Mo_2Cl_8$, $(NH_4)_5Mo_2Cl_9{\cdot}H_2O$, and $Rb_4Mo_2Cl_8$, all of which contain the discrete $Mo_2Cl_8{}^{4-}$ ion, have been observed by irradiating each complex with 514.5-nm Ar^+ excitation. This laser line approximately coincides with an electronic band maximum of the anion centered at ca. 19,000 cm^{-1}. Two overtone progressions in the metal–metal stretching frequency, ν_1(MoMo) a_{1g}, have been observed under these conditions to reach $11\nu_1$ for the first and $\nu_4 + 4\nu_1$ for the second, where ν_4 is probably the ν_2(MoCl) a_{1g} fundamental. The spectroscopic constants ω_1, x_{11}, and (less accurately) x_{14}, have been determined for the anion in each crystalline lattice. The relative intensities of the overtones to the fundamental are shown to depend on the exciting wavelength and also to decrease and the half-bandwidths to increase with increase in vibrational quantum number. Diffuse reflectance studies on the complexes have revealed a further weak electronic transition centered at ca. 6250 cm^{-1} which displays vibrational structure at room temperature. The electronic spectrum of the $Mo_2Cl_8{}^{4-}$ ion is discussed in the light of these new experimental results.

Rigorous resonance Raman (RR) spectra have recently been reported not only for the halogen gases[2] but also for a large number of tetraatomic and bigger inorganic molecules and ions.[3-11] In all cases, these spectra were observed when the exciting frequency fell within the contour of an allowed transition of the scattering species. The compound $K_4Mo_2Cl_8$ has also been found to display a RR spectrum when irradiated with 514.5-nm Ar^+ excitation, a wavelength which virtually coincides with the maximum of a strong electronic transition of the anion at 19,000 cm^{-1}. The original spectrum of Angell et al.,[12] as corrected and improved upon by Clark and Franks,[13] was characterized by the appearance of five harmonics of the ν_1 (MoMo) stretching fundamental, which occurs at 346 cm^{-1}. This

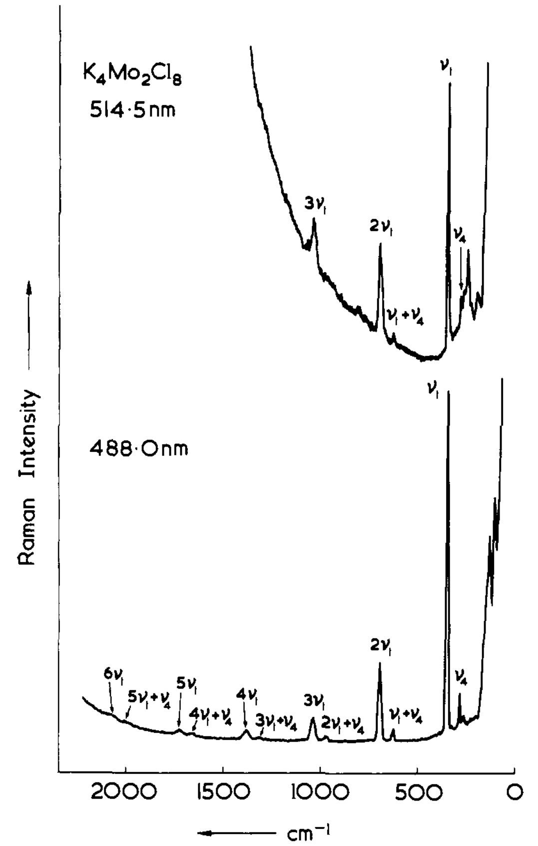

Figure 1. Resonance Raman spectra of the complex $K_4Mo_2Cl_8$ obtained with Ar^+ 514.5- and 488.0-nm excitation, slit widths 200/300/200 μm.

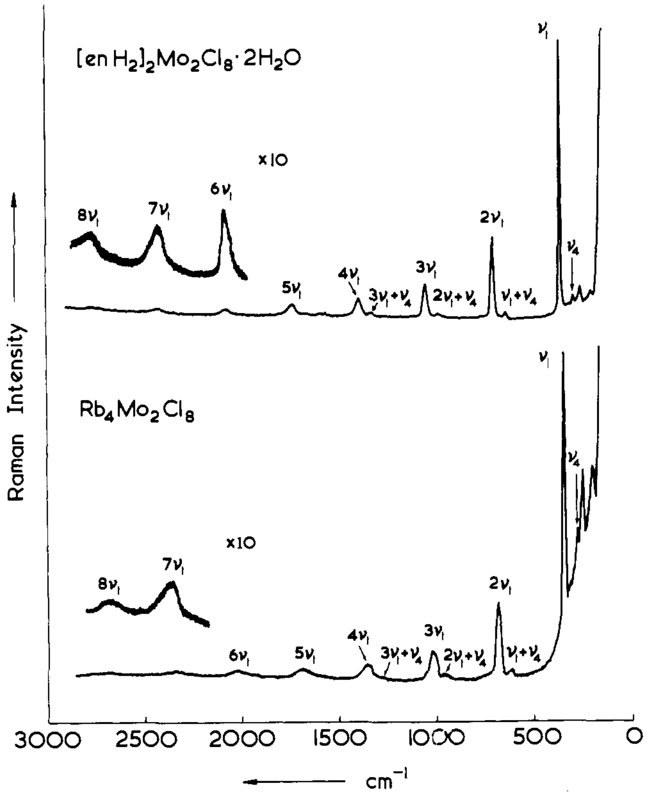

Figure 2. Resonance Raman spectra of $(enH_2)_2Mo_2Cl_8{\cdot}2H_2O$ and $Rb_4Mo_2Cl_8$ obtained with Ar^+ 514.5-nm excitation, slit widths 200/300/200 μm.

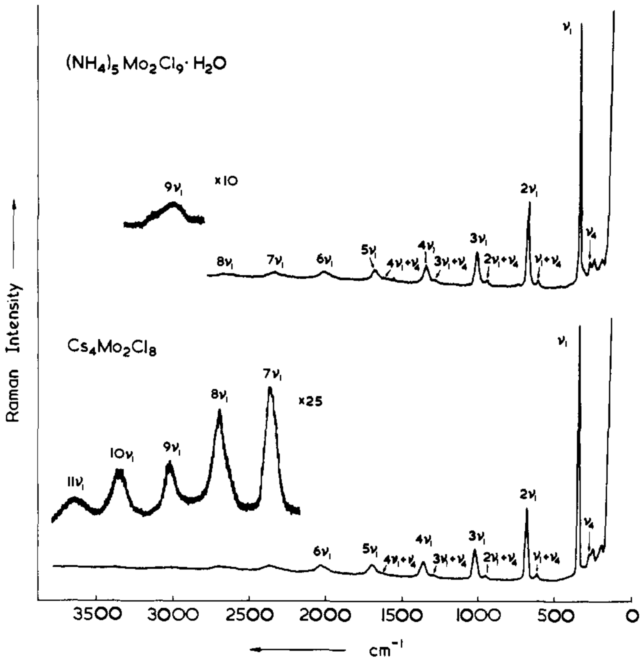

Figure 3. Resonance Raman spectra of $(NH_4)_5Mo_2Cl_9{\cdot}H_2O$ and $Cs_4Mo_2Cl_8$ obtained with Ar^+ 514.5-nm excitation, slit widths 200/300/200 μm.

spectrum has now been improved upon further, and, in addition, RR spectra have been observed from four other salts of the $Mo_2Cl_8^{4-}$ ion. Two overtone progressions have now been observed for each ion, extending at most as far as $11\nu_1$ for the first and $\nu_4 + 4\nu_1$ for the second. These long overtone progressions have permitted the accurate determination of the spectroscopic constants ω_1 and x_{11} for each complex anion, and hence an assessment of the influence of the lattice thereon. The observation of RR spectra from the $Mo_2Cl_8^{4-}$ ion in this way makes it clear that the 19,000-cm^{-1} electronic transition must be electric dipole allowed. This conclusion is discussed with reference to earlier work on this and related ions.[13-16]

Experimental Section

Preparation of Samples. The ethylenediamine (en), ammonium, and potassium salts were prepared by published methods.[17]

The rubidium salt was prepared by treating dimolybdenum tetraacetate (0.5 g) with rubidium chloride (1.14 g) in concentrated hydrochloric acid (25 ml). The mixture was shaken for 1 hr at 25°, after which time the violet precipitate was filtered off, washed with two 10-ml portions of absolute ethanol, and dried under vacuum at 25°, yield 0.8 g (85%). Anal. Calcd for $Rb_4Mo_2Cl_8$: Cl, 34.7. Found: Cl, 35.1.

The cesium salt was prepared similarly, yield 1.1 g (90%). Anal. Calcd for $Cs_4Mo_2Cl_8$: Cl, 28.2. Found: Cl, 28.5. Attempts to prepare calcium(II) and tetraethylammonium derivatives of the $Mo_2Cl_8^{4-}$ ion were not successful.

Instrumentation. The Raman spectra were recorded by use of a Spex 1401 spectrometer in conjunction with Coherent Radiation Model 52 Ar^+ and Kr^+ lasers. The scattered radiation was collected at 90° and focused by a f/0.95 lens onto the entrance slit of the monochromator after having been passed through a polarization scrambler. The 0.75-m Czerny-Turner monochromator employed two 1200 lines/mm Bausch and Lomb gratings blazed at 500 nm. The method of detection was photon counting in conjunction with a cooled, grade I, RCA C31034 phototube (linear display). The power available at 488.0, 514.5, 568.2, and 647.1 nm was 1.5 W, 1.8 W, 100 mW, and 500 mW, respectively. The spectra were calibrated by reference to the emission lines of neon which were superimposed directly onto the spectra while they were being recorded.

The rotating sample technique[18,19] was used in order to minimize thermal decomposition of the sample.

Table I. Wave Numbers[a] and Half-Bandwidths of the ν(MoMo), $\nu_1(a_{1g})$, Fundamental and Its Overtones of the $Mo_2Cl_8^{4-}$ Ion in Different Crystal Lattices Using 514.5-nm Excitation

Band	$(enH_2)_2Mo_2Cl_8\cdot 2H_2O$		$K_4Mo_2Cl_8$[b]		$Cs_4Mo_2Cl_8$		$(NH_4)_5Mo_2Cl_9\cdot H_2O$		$Rb_4Mo_2Cl_8$	
	Max	$\Delta\nu_{1/2}$	Max	$\Delta\nu_{1/2}$	Max	$\Delta\nu_{1/2}$	Max	$\Delta\nu_{1/2}$	Max	$\Delta\nu_{1/2}$
ν_1	347.8	9.4	345.9	11.1	340.4	11.8	338.0	10.2	337.9	14.9
$2\nu_1$	694.7	16.2	691.8	17.1	680.2	21.8	674.5	18.3	675.3	29.0
$3\nu_1$	1039.5	26.2	1035.4	22.8	1018.1	30.5	1009.1	28.4	1009.9	40.5
$4\nu_1$	1385	34	1378	29.4	1356.5	42	1344	39	1346	57
$5\nu_1$	1727	44	1720	38	1691	54	1674	54	1682	73
$6\nu_1$	2070	57	2060	50	2025	66	2006	75	2016	82
$7\nu_1$	2414	86			2358	86	2334	105	2348	103
$8\nu_1$	2753	125			2688	113	2658	160	2680	125
$9\nu_1$					3020	140	2984	230		
$10\nu_1$					3350	150				
$11\nu_1$					3675	210				

[a] Confirmed by use of 488.0-nm excitation. [b] Five overtones observable only with 488.0-nm excitation.

Table II. Relative Intensities[a] of the ν(MoMo), $\nu_1(a_{1g})$, Fundamental to Its Overtones of the $Mo_2Cl_8^{4-}$ Ion in Different Crystal Lattices as a Function of the Exciting Wavelength (nm)

Band	$(enH_2)_2Mo_2Cl_8\cdot 2H_2O$			$K_4Mo_2Cl_8$		$Cs_4Mo_2Cl_8$			$(NH_4)_5Mo_2Cl_9\cdot H_2O$			$Rb_4Mo_2Cl_8$		
	488.0	514.5	568.2	488.0	514.5	488.0	514.5	568.2	488.0	514.5	568.2	488.0	514,5	568,2
ν_1	1.0	1.0	1,0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
$2\nu_1$	0.31	0.42	0.50	0.31	0,57	0,34	0.55	0.46	0.33	0.50	0.48	0.44	0.49	0.54
$3\nu_1$	0.12	0,34	0.26	0.11	0,29	0.14	0.32	0.27	0.16	0.33	0.23	0.20	0.28	0,18
$4\nu_1$	0.04	0.21		0.06		0,06	0.26	0.12	0.09	0.21		0.09	0.19	
$5\nu_1$	0.02	0,15		0.03		0.03	0.21		0.07	0.12		0.07	0.09	
$6\nu_1$	0.02	0.09		0,01		0.01	0.18		0.04	0.09		0.03	0.10	
$7\nu_1$	0.01	0.07				0.01	0,18		0.03	0.04		0.02	0.05	
$8\nu_1$		0.06					0.15		0.02	0.02			0.03	
$9\nu_1$							0.08			0.01				
$10\nu_1$							0.06							
$11\nu_1$							0.05							

[a] Corrected for spectral response.

Band areas were determined by the cut-and-weigh procedure and then corrected for the relative spectral response of the instrument as described previously.[20]

The diffuse reflectance spectra of the powdered solids were recorded by use of a Cary 14 spectrometer.

X-Ray powder photographs of the potassium, rubidium, and cesium complexes were taken with a Guiner quadrupole focusing camera with copper Kα radiation. None of the compounds was isomorphous with any other.

Results and Discussion

Raman Spectra. The Raman spectrum of each salt of the $Mo_2Cl_8^{4-}$ ion is found to depend markedly on the wave number (ν_0) of the exciting line. With the 647.1-nm exciting line, whose wave number is less than that of the origin of the nearest electronic transition of the ion (17,897 cm^{-1}),[15] a normal Raman spectrum is obtained. However, for higher energy exciting lines, viz, those at 514.5 or 488.0 nm, excitation is within the envelope of this electronic band. Indeed, 514.5 nm corresponds closely to the electronic band maximum (see later). In consequence, as indicated in the introductory section, a RR spectrum might be expected to be observed with 514.5-nm excitation and (rather less effectively) with 488.0-nm excitation (owing to its less good resonance with the electronic band maximum).

The present results (Figures 1-3) bear out this expectation. RR spectra have been observed for all five salts studied, these being characterized in each case by an enormous enhancement to the intensity of the molybdenum-molybdenum stretching mode, ν_1(MoMo) a_{1g}, and the appearance of an overtone progression in ν_1. The progressions have been observed to reach $8\nu_1$, $6\nu_1$, $11\nu_1$, $8\nu_1$, and $9\nu_1$ for the enH_2^{2+}, K^+, Cs^+, NH_4^+, and Rb^+ salts, respectively. The wave numbers and half-bandwidths of the ν_1(MoMo) fundamental and its overtones are given in Table I, and the relative intensities of this fundamental of each complex to its overtones are given in Table II.

In agreement with the theory of Nafie et al.,[21] it is a totally symmetric fundamental which displays the RR effect. Moreover, the overtones in each case display the characteristic features[2] of the RR effect of continuous increase in half-bandwidth and continuous decrease in band area with increase in the vibrational quantum number. Similar effects have been observed previously for RR spectra of, for example, the MnO_4^- and CrO_4^{2-} ions[4] and titanium tetraiodide,[6] and the matter has been discussed theoretically by Kobinata.[22]

It is interesting that although 568.2-nm excitation (17,595 cm^{-1}) corresponds to 302 cm^{-1} less than the origin of the electronic transition under discussion, a RR spectrum of the $Mo_2Cl_8^{4-}$ ion may nevertheless be excited thereby. This is because a substantial proportion of ions exist at room temperature in vibrationally excited states with $\nu >$ 302 cm^{-1}, and thus these ions may give rise to the observed RR spectrum.

A second, weaker progression ($\nu_4 + v_1\nu_1$) is also evident in the spectrum of each complex out as far as $v_1 = 4$ for the ammonium salt and $v_1 = 3$ for each of the other complexes. The frequencies and half-bandwidths of each member of this progression are given in Table III for each complex. The fundamental ν_4, at 269.6-279.9 cm^{-1}, must be (from its wave number) a metal-chlorine stretching vibration, and as it is Raman active it must belong to one of the symmetry species a_{1g}, b_{1g}, or e_g (Table IV). On intensity grounds, the a_{1g} assignment is preferred. Thus ν_4 is probably the ν_2(MoCl) a_{1g} fundamental, but as this could not be established for certain, the fundamental is designated ν_4 in this paper.

Measurements of the depolarization ratio of the ν_4 band

Table III. Wave Numbers and Half-Bandwidths of the Members of the $\nu_4 + \nu_1\nu_1$ Progression for the $Mo_2Cl_8^{4-}$ Ion in Different Crystal Lattices (514.5-nm Excitation)

Band	$(enH_2)_2Mo_2Cl_8 \cdot 2H_2O$ Max	$(enH_2)_2Mo_2Cl_8 \cdot 2H_2O$ $\Delta\nu_{1/2}$	$K_4Mo_2Cl_8$[a] Max	$K_4Mo_2Cl_8$[a] $\Delta\nu_{1/2}$	$Cs_4Mo_2Cl_8$ Max	$Cs_4Mo_2Cl_8$ $\Delta\nu_{1/2}$	$(NH_4)_5Mo_2Cl_9 \cdot H_2O$ Max	$(NH_4)_5Mo_2Cl_9 \cdot H_2O$ $\Delta\nu_{1/2}$	$Rb_4Mo_2Cl_8$ Max	$Rb_4Mo_2Cl_8$ $\Delta\nu_{1/2}$
$\nu_4 + \nu_1$	627.4	19	621.9	14	609.7	20	611.6	16	607.2	24
$\nu_4 + 2\nu_1$	974.4	29	966.1	20	948.1	28	948.3	30	945.3	36
$\nu_4 + 3\nu_1$	1320	37	1308.7	32	1285	45	1282	55	1280	51
$\nu_4 + 4\nu_1$			1650	50			1613	83		

[a] Obtained using 488.0-nm excitation.

Table IV. The Distribution of the Normal Modes of Vibration of Ions of the Type $Mo_2Cl_8^{4-}$ (D_{4h} symmetry)[a]

	Approximate description								
	a_{1g} R(ρ)	b_{1g} R	b_{2g} R	e_g R	a_{1u}	a_{2u} ir	b_{1u}	b_{2u}	e_u ir
ν(MoMo)	1								
ν(MoCl)	1	1		1		1		1	1
δ(MoMoCl)	1[b]	1		1		1[b]		1	1
δ(ClMoCl)	1[b]		1	1		1[b]	1		1
MoMo torsion					1				

$\Gamma_{vib} = 3a_{1g} + 2b_{1g} + b_{2g} + 3e_g + a_{1u} + 2a_{2u} + b_{1u} + 2b_{2u} + 3e_u$

[a] The average bond parameters are Mo–Mo = 2.14 Å, Mo–Cl = 2.45 Å, and ∠(Mo–Mo–Cl) = 105°. [b] The symmetry species a_{1g} and a_{2u} each contain one redundancy in the angle bending coordinates.

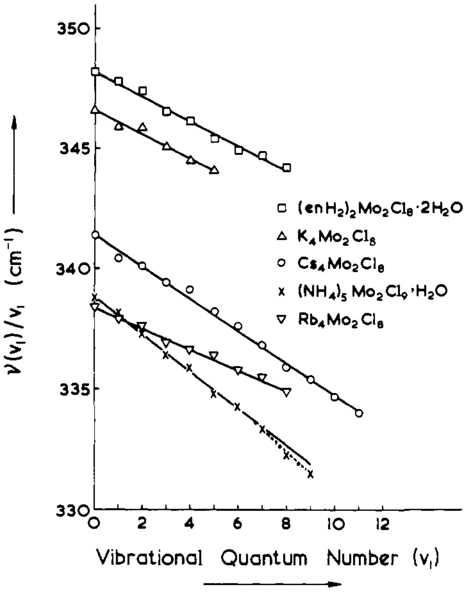

Figure 4. Plot of $\nu(v_1)/v_1$ vs. v_1 for ν(MoMo) of $(enH_2)_2Mo_2Cl_8 \cdot 2H_2O$, $K_4Mo_2Cl_8$, $Cs_4Mo_2Cl_8$, $(NH_4)_5Mo_2Cl_9 \cdot H_2O$, and $Rb_4Mo_2Cl_8$.

should allow a distinction to be drawn between the a_{1g} species on the one hand and the b_{1g} or e_g species on the other. However, the compound was not found to be both stable and soluble in any solvent tried. Even in concentrated hydrochloric acid saturated with hydrogen chloride and sealed under vacuum, aquation appears to be instantaneous. Such solutions display Raman bands (at 355.7, 708.5, 1056.8, and 1404.7 cm^{-1} with 488.0- and 514-5-nm excitation) which have steadily decreasing intensities and increasing half-bandwidths with increasing vibrational quantum number. These bands are, however, at significantly different frequencies from those characteristic of the $Mo_2Cl_8^{4-}$ ion, clearly demonstrating that this ion is not present in solution. However, the Mo_2^{4+} entity is undoubtedly preserved therein owing to the appearance of the RR spectrum mentioned above with laser lines approximately coinciding in frequency with the 19,500-cm^{-1} electronic band maximum of the solution. The actual species present in the solution is a chloroaquo one as discussed recently by Bowen and Taube.[23] This same solution, sealed under vacuum, apparently undergoes a further slow hydrolysis step as evidenced by the decay of the 19,500-cm^{-1} electronic band and the rise of a new band at 23,600 cm^{-1} over a period of months.

Harmonic Frequencies and Anharmonicity Constants. The observation of large numbers of overtones of the ν_1(MoMo) a_{1g} fundamental in the RR spectra of each complex makes it possible to determine accurately the harmonic frequency (ω_1) and anharmonicity constant (x_{11}). The observed wave number $\nu(v_1)$ of any overtone of an anharmonic oscillator is given by the expression[24]

$$\nu(v_1) = G(v_1) - G(0) = v_1\omega_1 - x_{11}(v_1^2 + v_1) + \dots$$

where $G(v_1)$ is the term value of the v_1th vibrational level. Thus ω_1 and x_{11} may be determined from a plot of $\nu(v_1)/v_1$ vs. v_1. The experimental results for each complex are illustrated in Figure 4, and the results of the least-squares analyses are summarized in Table V. The ω_1 values all lie in the range 348.7-338.8 cm^{-1}, and fall in the order $enH_2^{2+} > K^+ > Cs^+ > NH_4^+ > Rb^+$.

All the x_{11} values are very small, with 0.59 ± 0.17 encompassing them all; small x_{11} values appear to be a common feature of the RR effect. The differences between the x_{11} values found for some of the salts (e.g., rubidium and ammonium) appear to be significant, but the reason for the difference is not obvious.

Values for ω_1 and x_{11} may also be deduced from the frequencies of the members of the $\nu_4 + v_1\nu_1$ progression by plotting $[(\nu_4 + v_1\nu_1) - \nu_4]/v_1$ vs. v_1. This plot is also a straight line, which leads directly to the ω_1 and x_{11} values given in Table V. These values are not as accurate as those obtained from the main progression owing to the lower intensities of the bands, the fewer members observed, and the larger half-bandwidths for given vibrational quantum number v_1. The x_{11} values so obtained (0.60 ± 0.18 encompasses them all) are not significantly different from those deduced for the $v_1\nu_1$ progression. However, the ω_1 value derived from the $v_1\nu_1$ progression is, on average, 0.5 cm^{-1} bigger than that derived from the $\nu_4 + v_1\nu_1$ progression. This difference represents a direct measure, albeit not very precise, of the cross term x_{14} in the expression for the vibrational energy. Thus x_{14} is closely similar in magnitude to x_{11}.

The overtone progression observed for the Mo_2^{4+} entity in hydrochloric acid solutions (see previous section) leads similarly to ω_1 and x_{11} values of 358 ± 0.7 and 1.5 ± 0.7 cm^{-1}, respectively, i.e., values which are similar to, but significantly different from, those found for this entity as it exists as part of the $Mo_2Cl_8^{4-}$ ion.

Infrared Spectra. The infrared spectra of the complexes in the 400-20-cm^{-1} range are given in Table VI together with suggested band assignments.[2] Also included in this table are the wave numbers of the observed Raman bands in the fundamental region. Factor group splittings of some of the bands complicate the infrared spectra of the complexes, as also does the appearance of lattice bands (not clearly

Table V. Harmonic Frequencies and Anharmonicity Constants for the Different Salts of the $Mo_2Cl_8^{4-}$ Ion (cm^{-1})

Complex	$\nu_1\nu_1$ progression ω_1	$\nu_1\nu_1$ progression x_{11}	$\nu_4 + \nu_1\nu_1'$ progression ω_1	$\nu_4 + \nu_1\nu_1'$ progression x_{11}
$(enH_2)_2Mo_2Cl_8 \cdot 2H_2O$	348.7 ± 0.4	0.52 ± 0.06	348.4 ± 0.5	0.45 ± 0.07
$K_4Mo_2Cl_8$	347.1 ± 0.3	0.50 ± 0.05	346.5 ± 0.5	0.60 ± 0.08
$Cs_4Mo_2Cl_8$	342.1 ± 0.3	0.66 ± 0.07	341.3 ± 0.6	0.70 ± 0.11
$(NH_4)_5Mo_2Cl_9 \cdot H_2O$	339.6 ± 0.3	0.76 ± 0.07	339.2 ± 0.5	0.78 ± 0.13
$Rb_4Mo_2Cl_8$	338.8 ± 0.4	0.43 ± 0.05	338.5 ± 0.5	0.45 ± 0.07

Table VI. *Infrared and Raman Bands in the Spectra of Different Salts of the* $Mo_2Cl_8^{4-}$ Ion (cm^{-1})

	enH_2^{2+} salt		K^+ salt		Cs^+ salt		NH_4^+ salt		Rb^+ salt	
Assignment	R	Ir	R	Ir	R	Ir	R	Ir	R	Ir
ν(MoMo)	347,8 s		345.9 s		340.4 s	336 w, sh?	338,0 s		337.9 s	
	315.3 m		315.6 vw				305.4 m	308 m, sh	291.9 ms	
	303.8 m				286,9 m	295 vs		296 vs		309 sh
		294 vs		307 vs		286 s		288 s		295 s
ν(MoCl)	279.9 m[a]		276.7 m[a]		269.8 m[a]		274.0 m[a]		269.6 m[a]	
		272 m		275 m		272 w	269.9 m	265 m		266 w
	256.9 m		252.8 m		242.5 m	260 sh	256.7 w		240.2 m	
					230.2 m					
Skeletal bends	200.1 w		191,1 w	182 s	186.5 w		192.9 w	195 vs, br	189.3 w	184 vw, sh
	188.2 w	176 s, br		160 m		161 s				164 ms
		ca. 110 w, br		130 m		126 vw?		128 w		127 vw
		113 wm		113 wm						112 vw
Lattice?										96 vw
		97 w		91 wm		76 m				88 w
				68 vw				58 vw		79 w

[a] Designated ν_4 in this paper.

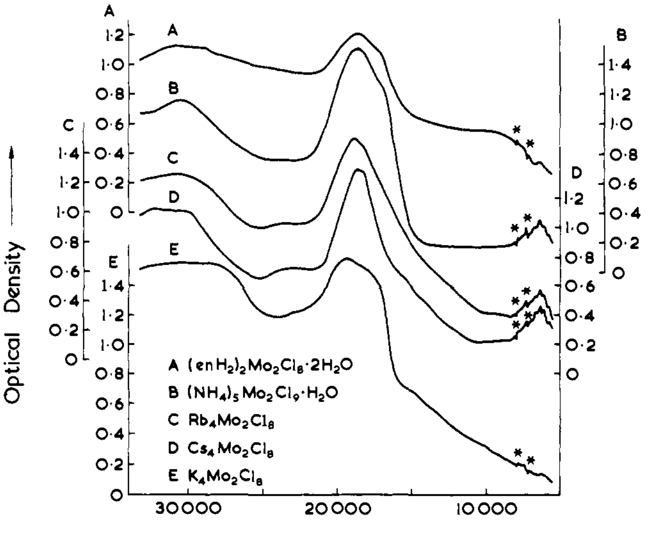

Figure 5. Diffuse reflectance spectra of (A) $(enH_2)_2Mo_2Cl_8 \cdot 2H_2O$, (B) $(NH_4)_5Mo_2Cl_9 \cdot H_2O$, (C) $Rb_4Mo_2Cl_8$, (D) $Cs_4Mo_2Cl_8$, and (E) $K_4Mo_2Cl_8$. The asterisks mark the positions of background peaks (possibly arising from adsorbed water vapor on the magnesium carbonate blocks).

separable from fundamentals of the anion). Detailed discussion of the infrared spectra of the complexes is therefore not given.

Electronic Spectra. The diffuse reflectance spectra of each of the five salts of the $Mo_2Cl_8^{4-}$ ion studied are shown in Figure 5. The common features in the visible-uv region are strong bands centered at ca. 19,000 and 28,000-32,000 cm^{-1}, together with some smaller features. The actual maximum of the 19,000-cm^{-1} band shifts very slightly to higher wave numbers in the order $EnH_2^{2+} < NH_4^+ < Rb^+ < Cs^+ < K^+$. However, it seems improbable that this shift is of any significance with respect to the RR spectra, because the center of gravity of this band appears to be 18,700 ± 200 cm^{-1} in all cases. Moreover it is common to observe a background in diffuse reflectance spectra which rises toward the uv. On the other hand, it may be significant that the longest RR progression is observed for the Cs^+ salt, which has the smallest half-bandwidth (ca. 2600 cm^{-1}) whereas the shortest RR progression is found for the K^+ salt, which has the largest half-bandwidth (ca. 5000 cm^{-1}). On the assumption of a constant oscillator strength for this electronic transition in each salt, the extinction coefficient would accordingly be greatest for the Cs^+ salt, which would therefore be expected to display the most pronounced RR spectrum.[25]

It is of considerable interest that the 5°K electronic spectrum of $K_4Mo_2Cl_8$ obtained by Cowman and Gray[15] reveals a richly structured system in the 19,000-cm^{-1} region, with the origin at 17,897 cm^{-1} and vibrational spacing of ca. 351 cm^{-1}. It is precisely this fundamental, ν_1(MoMo) a_{1g} (ground state value 346 cm^{-1}) which displays the RR effect when the laser frequency is made to coincide with the maximum of this electronic transition. Indeed, not even the first overtone of the other two totally symmetric vibrations of the $Mo_2Cl_8^{4-}$ ion, ν_2(MoCl) and ν_3(ClMoCl) (stretch and bend, respectively) could be observed. The rather surprising fact that the ground and excited state wave numbers for the ν_1(MoMo) fundamental are virtually identical may be attributed to a possible difference between the extent of mixing of the MoMo and MoCl stretching fundamentals in the two electronic states. The relative positions of relevant laser lines to the vibrational structure of the 19,000-cm^{-1} band are shown in Figure 6.

Extension of the diffuse reflectance studies to 5500 cm^{-1} (the limit of operation of the Cary 14 spectrometer in this mode of operation) revealed a hitherto unreported electronic transition centered at ca. 6250 cm^{-1} (Figure 7). The band was most apparent for the Cs^+, NH_4^+, and Rb^+ salts, and in each case it displayed a vibrational progression with average spacings of 298, 283, and 280 cm^{-1}, respectively (Table VII). Such progressions are invariably in totally symmetric fundamentals, which means (on account of the wave number) that the fundamental involved is either

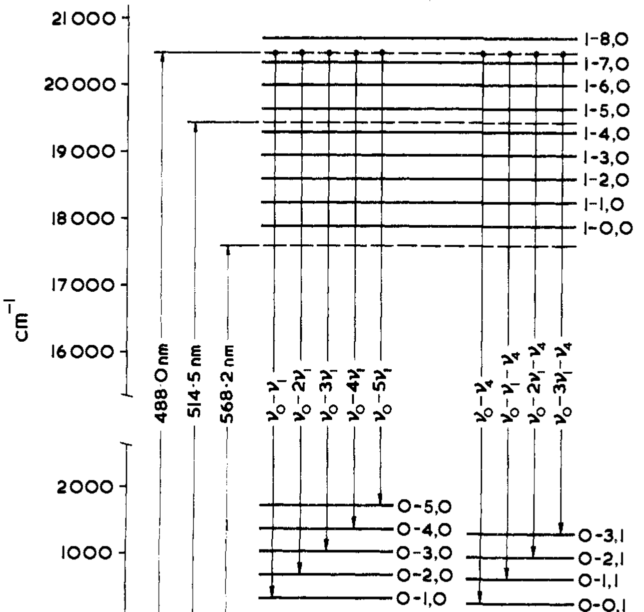

Figure 6. Relative positions of relevant laser lines to the vibrational structure in the 19,000-cm^{-1} excited electronic state. Transitions from the 488.0-nm intermediate state down to the ground electronic state indicate the two overtone progressions observed in the resonance Raman effect.

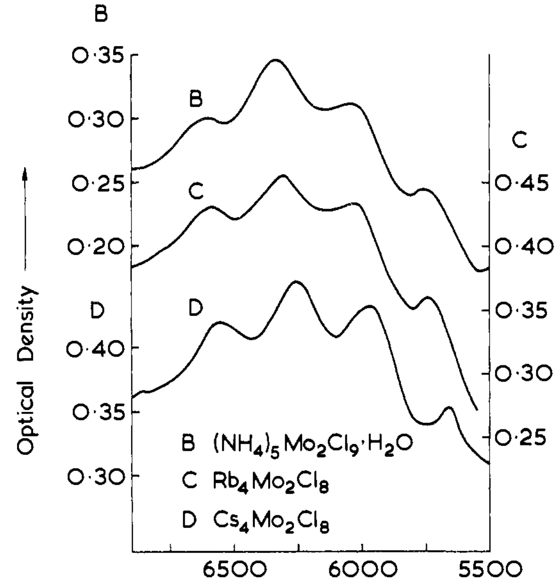

Figure 7. Detail of the diffuse reflectance spectra of (B) $(NH_4)_5Mo_2Cl_9{\cdot}H_2O$, (C) $Rb_4Mo_2Cl_8$, and (D) $Cs_4Mo_2Cl_8$ in the 6000-cm^{-1} region, showing the vibrational structure to the electronic transition.

ν_1(MoMo) a_{1g} or ν_2(MoCl) a_{1g}. If the former is the case, the fall in the average value of the wave number of the fundamental on change from the ground to the 6250-cm^{-1} excited state (340 → 297 cm^{-1}) is 15.6% which is a rather typical value (cf. for the MnO_4^- ion), the fall in the wave number of the a_1 fundamental on excitation to its 18,000-cm^{-1} state (845 → 755 cm^{-1})[26] is 10.7%. On the other hand, if the progression were in ν(MoCl) then the wave number of the fundamental must have *increased* on electronic excitation of the molecule (277 → 287 cm^{-1}) by 3.6%, which seems improbable.

Table VII. Vibrational Structural Data to the 6250-cm^{-1} Electronic Band of Different Salts of the $Mo_2Cl_8^{4-}$ Ion (cm^{-1})

$Cs_4Mo_2Cl_8$		$(NH_4)_5Mo_2Cl_9{\cdot}H_2O$		$Rb_4Mo_2Cl_8$	
Max	$\Delta\nu$	Max	$\Delta\nu$	Max	$\Delta\nu$
6557		6617		6588	
	297		280		278
6260		6337		6310	
	301		282		275
5959		6055		6035	
	297		287		286
5662		5768		5749	
	Av 298		Av 283		Av 280

In seeking an assignment for the 19000-cm^{-1} band of the $Mo_2Cl_8^{4-}$ ion, it is logical to seek guidance from the band assignments made for the isoelectronic and isostructural $Re_2Cl_8^{2-}$ ion. The lowest observed electronic transition of this ion (14,500 cm^{-1}) has been assigned,[27] on the basis of extended Huckel molecular orbital calculations, to the $^1a_{2u} \leftarrow {}^1b_{2g}$ (σ_n (1) ← δ) transition, which would be electric dipole forbidden. However, this calculation is now considered to be invalid, as also are some of the arguments used in discussing the energies of other possible transitions of the valence electrons. Cowman and Gray,[15] on the basis of polarized single-crystal work on the complex $Re_2Cl_6[P(C_6H_5)_3]_2$, which has a similar structure to, and the same number of valence electrons as the $Re_2Cl_8^{2-}$ ion, have concluded that the correct assignment of this transition is $2b_{1u} \leftarrow 2b_{2g}$ ($\delta^* \leftarrow \delta$), i.e., an electric dipole allowed transition of the Mulliken charge-transfer type.[28] This conclusion has now been substantiated by X_α scattered wave (SCF-X_αSW) calculations.[29] Likewise, earlier opinions[30] as to the assignment of the lowest hitherto observed electronic transition of dimolybdenum species have been displaced by SCF-X_αSW calculations on the electronic structure of the $Mo_2Cl_8^{4-}$ ion; these calculations demonstrate[31] that this transition should also be assigned thus: $2b_{1u} \leftarrow 2b_{2g}$ ($\delta^* \leftarrow \delta$). The present RR results are in agreement with this conclusion for the following reason. RR spectra have only been observed, and are only expected to be observed, from a scattering molecule when the laser frequency is brought into resonance with an electric dipole *allowed* transition,[32] and the $\delta^* \leftarrow \delta$ transition is undoubtedly the lowest such transition (calculated oscillator strength 0.22 for an MoMo distance of 2.11 Å).[33] Further, it seems highly significant that, of the three totally symmetric fundamentals of the $Mo_2Cl_8^{4-}$ ion, it is only ν(MoMo) which displays the RR effect. This is to be expected where the resonant electronic transition is localized on the metal-metal entity, and thus where this transition would lead to a change only (or primarily) in the metal-metal bond order.

It seems likely that the two electronic transitions observed in the infrared-visible region of the spectrum of this ion both arise from the $2b_{1u} \leftarrow 2b_{2g}$ ($\delta^* \leftarrow \delta$) one-electron transition, the 19,000-cm^{-1} band being the spin-allowed component $^1A_{2u} \leftarrow {}^1A_{1g}$ and the 6250-cm^{-1} band being the spin-forbidden component $^3A_{2u} \leftarrow {}^1A_{1g}$. The calculated values for these two transitions are 13,700 and 4800 cm^{-1}, respectively.[31] The intensity difference between spin-allowed and spin-forbidden transitions is not expected to be as dramatic for molybdenum as for most first-row transition metal ions, on account of the relatively large single-electron spin-orbit coupling constant (ζ_{nd}) for Mo^{2+} (695 cm^{-1})[34] which leads to violation of the $\Delta S = 0$ selection rule; cf. the electronic spectrum of K_3MoCl_6.[35] The observation of the 6250-cm^{-1} band for the Rb^+ and Cs^+ salts of the $Mo_2Cl_8^{4-}$ ion but not for the K^+ salt may likewise be associated with the larger spin-orbit coupling constants for the heavier counterions; however, the reason why the NH_4^+ salt but not the enH_2^{2+} salt exhibits this band is not clear but may be simply associated with the fact that each salt has a different crystal structure.

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The Structure of Heptakis(*tert*-butyl isocyanide)molybdenum(II) Hexafluorophosphate, a Seven-Coordinate Complex with C_{2v} Monocapped Trigonal Prismatic Geometry[1]

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Abstract: The structure of heptakis(*tert*-butyl isocyanide)molybdenum(II) hexafluorophosphate has been determined in a single-crystal X-ray diffraction study. The compound crystallizes in the monoclinic system. Refinement was carried out in the nonstandard space group $F2/m$ having a = 25.220 (10) Å, b = 11.665 (5) Å, c = 38.013 (17) Å, β = 90.42 (3)°, and Z = 4. The geometry of the seven-coordinate molybdenum(II) cation is that of a distorted capped trigonal prism of approximate C_{2v} symmetry. Deviations of the structure from idealized geometry (typified by the $[NbF_7]^{2-}$ ion) result largely from inequivalencies in the Mo–C bond lengths. These occur in three classes, viz., the Mo–C bond of the unique, capping ligand, 2.171 (9) Å, the four Mo–C bonds to the capped face, average 2.133 (7) Å, and the two Mo–C bonds opposite the capped face, 2.051 (7) Å. The structure bears many similarities to that of the related $[(t\text{-}C_4H_9NC)_6MoI]^+$ cation, in which the iodide ligand occupies the capped face of the trigonal prism. The stereochemistry of the C_{2v} monocapped trigonal prism is defined in terms of polyhedral shape parameters.

The number of structurally well-characterized seven-coordinate transition metal complexes has increased dramatically in the past several years.[3,4] Compounds containing only monodentate ligands are still rare,[5,6] however, and X-ray structural information about monomers with seven identical ligands is available only for $[ZrF_7]^{3-}$,[7] $[NbF_7]^{2-}$,[8] and $[V(CN)_7]^{4-}$.[9] Compounds of the last kind are interesting because they permit an analysis of the factors influencing the choice of geometry for a seven-coordinate complex in the absence of stereochemical constraints imposed by multidentate, chelating ligands. The paucity of X-ray structural data for discrete ML_7 complexes has recently been noted.[10]

During a study of the alkylation of silver octacyanomolybdate(IV),[2] a number of cationic molybdenum(II) isocyanide complexes were isolated, including $[Mo(CNR)_6I]^+$[11] and $[Mo(CNR)_7]^{2+}$,[12] where R = CH_3 or $t\text{-}C_4H_9$. These compounds, as well as $[Mo(CNR)_6X]^+$[13] and $Mo(CNR)_5X_2$, X = Cl or Br,[14] have also been obtained by halogen oxidation of molybdenum hexacarbonyl, a route that has long been known to produce seven-coordinate molybdenum(II) compounds.[15] The existence of X-ray quality crystals of $[Mo(CNR)_7]^{2+}$ and $[Mo(CNR)_6X]^+$, X = Cl, Br, or I, salts afforded an excellent opportunity to investigate the effects of charge, ligand size, and even crystal packing forces on the geometry of seven-coordinate d^4 mo