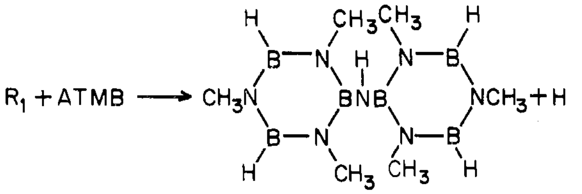
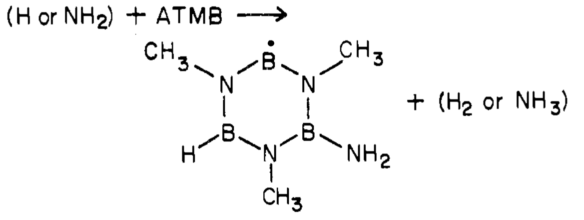


(12)

V

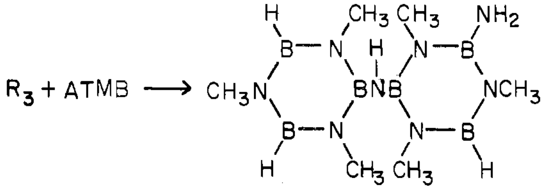
substituted diborazinyl amine VI is not clear. Reactions 13



(13)

R_3

and 14 represent one possible pathway.



(14)

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Registry No. *N*-Methylborazine, 21127-94-6; *N*-dimethylborazine, 23208-28-8; *N*-trimethylborazine, 1004-35-9; 1-methyl-2-aminoborazine, 54517-68-9; 1-methyl-4-aminoborazine, 54517-69-0; 1,3-dimethyl-2-aminoborazine, 54517-70-3; 1,3-dimethyl-4-aminoborazine, 54517-71-4; 1,3,5-trimethyl-2-aminoborazine, 54517-72-5; 1-methyl-2-methoxyborazine, 54517-73-6; 1-methyl-4-methoxyborazine, 54517-74-7; 2-methoxyborazine, 18277-68-4; 1-methyl-2-dimethylaminoborazine, 37013-94-8; 1-methyl-4-dimethylaminoborazine, 37133-10-1; 1,3,5-trimethyl-2-dimethylaminoborazine, 54517-75-8; 2-dimethylaminoborazine, 15127-53-4; 1,2-bis(3',5'-dimethylborazinyl)ethane, 54517-76-9; bis(1,3,5-trimethylborazinyl)amine, 54517-77-0; I, 253-18-9; II, 54517-22-5; III, 54517-23-6; VI, 54517-78-1; borazine, 6569-51-3; NH_3, 7664-41-7; CH_3OH, 67-56-1; $NH(CH_3)_2$, 124-40-3.

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Polarized Infrared and Raman Studies of Some Tri-μ-chloro-bis(trichlorochromate(III)) Single Crystals and Normal-Coordinate Analysis of the $Cr_2Cl_9^{3-}$ Ion

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The polarized infrared reflectance and Raman spectra of single crystals having the general formula $A_3Cr_2Cl_9$ (A = K, Rb, Cs) have been recorded at 300 and 77°K. Nearly all of the 30 fundamental modes of vibration, predicted by factor group analysis, are observed for each complex and unambiguously assigned to their respective symmetry species. A normal-coordinate analysis of the $Cr_2Cl_9^{3-}$ anion using a Urey–Bradley potential function produced calculated frequencies and symmetry species which gave good agreement with the vibrational data observed for the cesium complex.

Introduction

Although the vibrational spectra of dimetalate complexes having the general formula $A_3M_2X_9$ (A = alkali metal or tetraalkylammonium ion; M = Ti, Cr, Mo, W, Rh, Tl; X = Cl, Br) have been previously recorded,[2-8] the majority of this work has been concerned only with the infrared region down to 150 cm^{-1}. Recently more detailed studies of the infrared and Raman spectra of complexes containing $Cr_2Cl_9^{3-}$, $W_2Cl_9^{3-}$, and $Tl_2Cl_9^{3-}$ ions have been reported.[3,8] However, with the exception of a single-crystal Raman study on $Cs_3Tl_2Cl_9$[3] previous symmetry assignments have been based on spectral data obtained from powdered solids. This has led to the observation of far fewer bands than theoretically predicted and, in some cases, erroneous assignments.

There have been two previous reports of normal-coordinate analysis of complexes containing $M_2Cl_9^{3-}$ ions. Beattie et al.[3]

for the $Tl_2Cl_9^{3-}$ ion made no attempt to refine the force field which was based on intuitive transference of force constants from the $SnCl_6^{2-}$ ion. A more detailed analysis[8] of the $Cr_2Cl_9^{3-}$ and $W_2Cl_9^{3-}$ ions, relying on the assumption that bridge deformation constants can be directly transferred from the chromium to the tungsten complex, resulted in a value of 1.15 mdyn/Å for the W–W stretching force constant. Both calculations used a general valence force field and lattice interactions were not considered although in the latter case rather more interaction force constants were used.

We have recorded the polarized infrared reflectance and Raman spectra of single crystals having the formula $A_3Cr_2Cl_9$ (A = K, Rb, Cs) and assigned the observed bands to their respective symmetry species. Since, in certain cases, these assignments differed from those previously reported, the normal-coordinate analysis of the $Cr_2Cl_9^{3-}$ ion was repeated, though using the more restricted Urey–Bradley force field.

Experimental Section

All the complexes studied were prepared as large single crystals from the melt using the Stockbarger technique.[9] Stoichiometric quantities of the alkali metal chloride and anhydrous $CrCl_3$ were loaded, under an inert atmosphere, into a silica crucible which was then evacuated to 10^{-3} Torr and sealed. The crucible and its contents were heated to the melting point of the particular complex (melting points of the K,[10,11] Rb,[12] and Cs[12] complexes were taken as 813, 874, and 894°, respectively) and then lowered through a temperature gradient of 60°/in. at a rate of 2 mm/hr. The crystals thus obtained cleaved readily along $\{000\bar{1}\}$ and $\{10\bar{1}0\}$ planes and these faces were used for spectroscopic studies without further preparation. In view of the sensitivity of these complexes to moisture, storage and handling were carried out in a dry nitrogen atmosphere.

Polarized infrared reflectance spectra from 10 to 400 cm^{-1} were recorded at a resolution of 2.5 cm^{-1} on a Beckman RIIC FS 720 using an FTC 100 computer. The angle of incidence for reflectance was 12° and polarization of the incident radiation, to better than 98%, was obtained using an AIM wire grid polarizer. The instrument was calibrated against atmospheric water vapor. Low-temperature spectra were recorded using a Beckman RIIC VTL 2 cell, the temperature at the sample varying from 105 to 115°K as measured by a copper–constantan thermocouple.

Polarized Raman spectra were recorded using a 90° scattering geometry on a Spex Ramalog 4 spectrophotometer at a resolution of 2 cm^{-1}. The instrument was calibrated to ±1 cm^{-1} using the plasma lines of an argon laser. The 457.9-nm line of a Coherent Radiation 52G argon ion laser was used as the exciting source (60 mW at the sample) in preference to the more intense 488.0-nm line since the latter tended to "burn" the crystal surface. Crystal samples were mounted on the block of an evacuable cryostat thus enabling spectra to be recorded at room temperature and liquid nitrogen temperature without surface hydrolysis occurring.

The Kramers–Kronig analysis was obtained using an ICL KDF 9 computer while force constant calculations were performed on an IBM 370/155 computer.

Results

From X-ray powder studies the three complexes are known to be isomorphous[13] but detailed single-crystal structural data are only available for $Cs_3Cr_2Cl_9$ which is reported[14,15] to have the space group D_{6h}^4-$P6_3/mmc$ ($Z = 2$) and contains isolated $Cr_2Cl_9^{3-}$ ions. These ions, having D_{3h} symmetry, are in the form of two face-shared $CrCl_6$ octahedra and are situated in the crystal on sites also of D_{3h} symmetry. As a result of the site group symmetry the fundamental modes of vibration of the isolated $Cr_2Cl_9^{3-}$ ion will be unperturbed by the static crystal field effect but each mode will be split into a "g" and "u" component arising from correlation coupling (dynamic crystal field effect) between the two ions in the unit cell. Because the vibrational selection rules depend upon the factor group, D_{6h}, this correlation coupling, shown in Table I, will only be observed for the E' modes of the isolated ion.

Table I. Correlation Table for $Cr_2Cl_9^{3-}$ Ions in $A_3Cr_2Cl_9$ Complexes with the D_{6h}^4 Space Group

Free ion and site symmetry, D_{3h}	Unit cell, D_{6h}
4 A_1'	4 A_{1g}[a]
	4 B_{2u}
A_2'	A_{2g}
	B_{1u}
5 E'	5 E_{2g}[a]
	5 E_{1u}[b]
A_1''	B_{2g}
	A_{1u}
3 A_2''	3 B_{1g}
	3 A_{2u}[b]
4 E''	4 E_{1g}[a]
	4 E_{2u}

[a] Raman active. [b] Infrared active.

Table II. Factor Group Analysis of $A_3Cr_2Cl_9$ Complexes with Space Group D_{6h}^4 [a]

D_{6h}	n_i	T	T'	R	n_i'	Activity
A_{1g}	5		1		4	$x^2 + y^2, z^2$
A_{2g}	2			1	1	
B_{1g}	6		3		3	
B_{2g}	1				1	
E_{1g}	6		1	1	4	xz, yz
E_{2g}	8		3		5	$x^2 - y^2, xy$
A_{1u}	1				1	
A_{2u}	6	1	2		3	z
B_{1u}	2			1	1	
B_{2u}	5		1		4	
E_{1u}	8	1	2		5	x, y
E_{2u}	6		1	1	4	

[a] n_i = total number of modes; T = number of acoustic modes; T' = number of translatory lattice modes; R = number of rotatory lattice modes; n_i' = number of internal modes.

In addition to the internal modes of vibration associated with the $Cr_2Cl_9^{3-}$ ions, the number of infrared- and Raman-active translatory lattice modes, corresponding to a vibration of the cations against the polyatomic anions, is given by the representation

$$\Gamma_{\text{lattice}} = A_{1g} + 3\ E_{2g} + E_{1g} + 2\ A_{2u} + 2\ E_{1u} \tag{1}$$

There is also a rotatory lattice mode of E_{1g} symmetry which constitutes a slight torsional motion of the $Cr_2Cl_9^{3-}$ ion. The number and symmetry species of these optically active lattice modes were derived from a factor group analysis based upon the proposed space group and this is presented in Table II. From this it can be seen that a total of 19 bands should be observed in the Raman spectra and 12 in the infrared spectra of $Cs_3Cr_2Cl_9$.

The frequencies, in cm^{-1}, of the observed infrared and Raman bands, the symmetries of the crystal modes, and corresponding free ion modes for the three complexes are given in Table III. For convenience each free ion mode is described in terms of the internal symmetry coordinate that contributes most to its potential energy. Because of the increase in the signal to noise ratio and significant reduction of the half-bandwidth which aided the observation of weak spectral features, Raman spectra were recorded at liquid nitrogen temperatures. Compared with the spectra recorded at ambient temperature the only difference was an increase in frequency of 3–5 cm^{-1} of those bands primarily associated with the terminal and bridging Cr–Cl stretching vibrations; certainly no changes were observed which could be attributed to any kind of phase transition. Apart from frequency differences the Raman spectra of all three complexes were almost identical

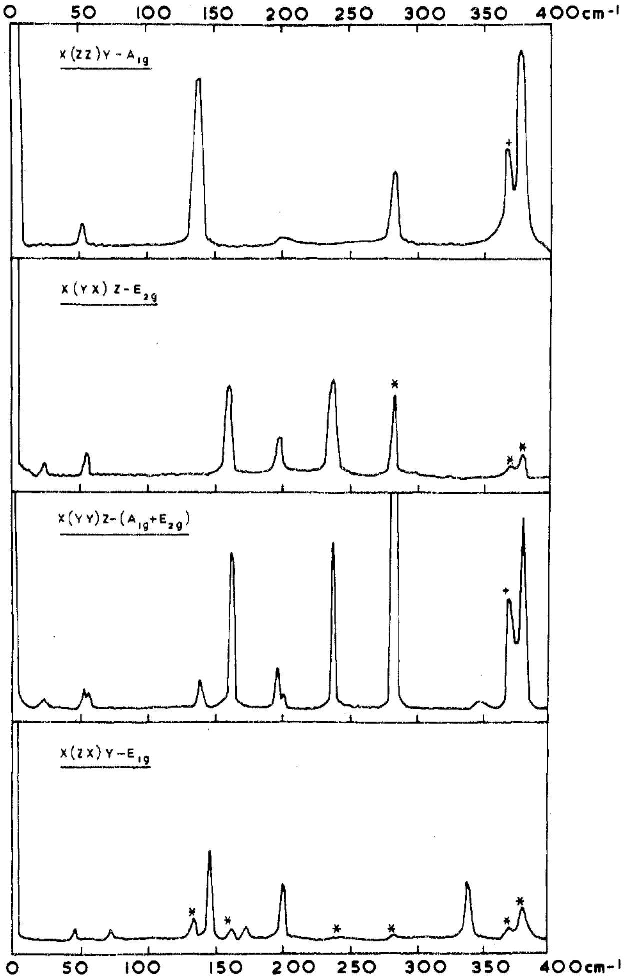

Figure 1. Single-crystal Raman spectra of $Cs_3Cr_2Cl_9$ (recorded at −196°): *, bands of different symmetry due to polarization leakage; +, overtone band.

and those for $Cs_3Cr_2Cl_9$ are shown in Figure 1 with the relative intensity data given in Table IV; the method of indicating the geometry used to obtain scattering from individual tensor components is that of Damen, Porto, and Tell.[16]

The polarized infrared reflectance spectra were recorded at both ambient and low temperatures and similar trends to those already mentioned for the Raman spectra were noted; the spectral features for all three complexes were almost identical and the stretching modes increased in frequency by about 4 cm^{-1} on cooling the sample. Typical of these infrared spectra are those for $Cs_3Cr_2Cl_9$ shown in Figure 2 where the E_{1u} and A_{2u} modes were recorded for the ordinary and extraordinary rays, respectively.

In ionic crystals it is well established that, due to dielectric dispersion, infrared reflectance maxima do not correspond with the true vibrational (oscillator) frequencies and therefore reflectivity data are normally analyzed.

Using the Kramers-Kronig (K–K) relationship[17,18]

$$\theta_\nu = \frac{2\nu}{\pi}\int_0^\infty \frac{\ln\,[r(\nu_0)]}{\nu^2 - \nu_0^2}\,d\nu_0 \qquad (2)$$

(where $r = R^{1/2}$, θ is the phase difference between the incident and reflected radiation, and R is the reflectivity) the variation of the real (ϵ') and imaginary (ϵ'') parts of the dielectric constant with frequency was obtained. The maxima in ϵ'', which correspond to the true oscillator frequencies, were found to occur at higher frequencies (1–3 cm^{-1}) than the observed reflectance maxima which is indicative of slight errors in the values taken for R. These errors may be attributed to deterioration of the cleared faces, caused by hydrolysis, during the transference of the crystal to the spectrophotometer and subsequent alignment with the result that accurate values for the reflectivity could not be obtained. However, the K–K analysis was sufficiently reliable to show that dispersion effects were small and hence the infrared values listed in Table III were determined using the approximation[19] where the oscillator frequency is taken at the point of maximum slope on the low-frequency side of the reflectance band.

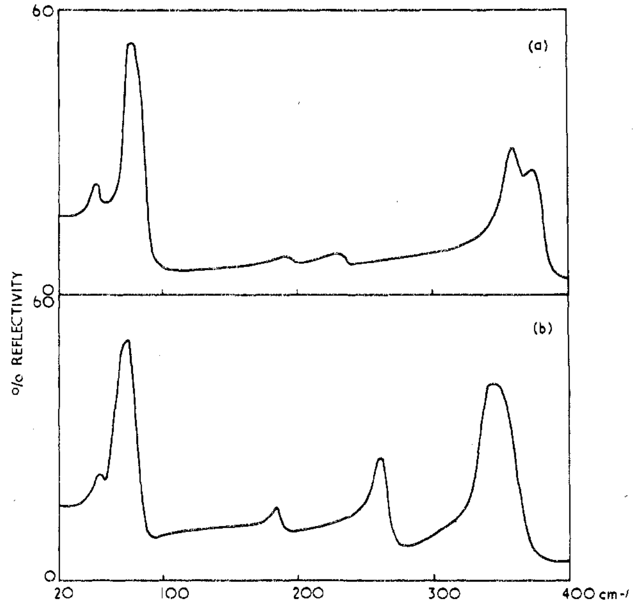

Figure 2. Polarized infrared reflectance spectra of $Cs_3Cr_2Cl_9$ (recorded at −196°): (a) ordinary ray, E_{1u} modes; (b) extraordinary ray, A_{2u} modes.

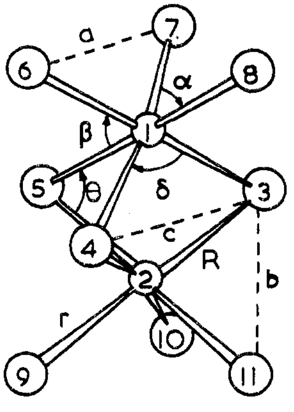

Figure 3. Internal coordinates for the $Cr_2Cl_9{}^{3-}$ Anion.

The effect of dielectric dispersion is most noticeable at about 370 cm^{-1} in the ordinary ray spectrum. In all three complexes there appear to be two strong reflectance bands in this region but from the ϵ'' spectrum these were found to consist of a strong band with a much weaker band at higher frequency. By comparison with other spectra exhibiting similar dispersion effects[20] the frequency of the weak band was taken as the minimum between the two reflectance bands.

Since the single-crystal data for these complexes resulted in symmetry assignments which differed significantly from those reported previously[8] the normal-coordinate analysis for the $Cr_2Cl_9{}^{3-}$ ion was repeated using the Urey–Bradley force field.[21] The potential energy in terms of the internal coordinates defined in Figure 3 is given by eq 3. The geometry of the $Cr_2Cl_9{}^{3-}$ ion was obtained from the crystal structure of $Cs_3Cr_2Cl_9$[14] and the potential energy matrix was symmetrized using cartesian symmetry coordinates.

Table III. Observed Infrared and Raman Spectra of the $A_3Cr_2Cl_9$ Complexes

	Assignments		Freq,[b] cm^{-1}		
Type of vibration	Free ion modes	Crystal modes	$K_3Cr_2Cl_9$	$Rb_3Cr_2Cl_9$	$Cs_3Cr_2Cl_9$
Terminal str	ν_1 A_1'	A_{1g}	393	388	378
	ν_8 E'	E_{1u}	369	364	346
		E_{2g}			346
	ν_{13} E''	E_{1g}	347	345	337
	ν_5 A_2''	A_{2u}	361	355	340
Bridging str	ν_2 A_1'	A_{1g}	299	293	283
	ν_6 A_2''	A_{2u}	266	263	256
a	ν_9 E'	E_{2g}	248	245	237
		E_{1u}	242	237	232
	ν_{14} E''	E_{1g}	202	200	199
Terminal bend	ν_3 A_1'	A_{1g}	206	205	200
a	ν_{10} E'	E_{2g}	195	197	196
		E_{1u}	195	195	190
Terminal bend	ν_7 A_2''	A_{2u}	186	185	184
a	ν_{15} E''	E_{1g}	179	178	172
	ν_{11} E'	E_{2g}	164	165	161
		E_{1u}			
$CrCl_3$ wag	ν_{16} E''	E_{1g}	144	146	145
Cr–Cl_3–Cr breathing	ν_4 A_1'	A_{1g}	141	145	138
$CrCl_3$ wag	ν_{12} E'	E_{2g}	86	94	
		E_{1u}	94	84	75
Lattice modes		E_{1g}	33	86	75
		A_{2u}	92	80	70
		E_{2g}	78	64	55
		A_{2u}	66	59	54
		E_{1u}	67	58	52
		A_{1g}	51	52	53
		E_{1g}	29	48	45
		E_{2g}		20	24
		E_{1u}			
		E_{2g}			
Overtone	$(2\nu_7)$	A_{1g}	378	376	368
Combination	$(\nu_4 + \nu_9, \nu_7 + \nu_{14}$ or $\nu_7 + \nu_{16})$	E_{1u}	374	371	368

[a] Complex mixture of terminal bend and bridging bend and stretch (see text). [b] Frequencies observed at low temperature.

Table IV. Single-Crystal Raman Polarization Data[a] for $CS_3Cr_2Cl_9$

	$x(zz)y$	$x(zx)y$	$x(yy)z$	$x(yx)z$	
378	138	11	168	31	A_{1g}
368	70	6	112	21	$(A_{2u}{}^2)$
346	0	0	5	0	E_{2g}
337	0	34	0	0	E_{1g}
283	50	7	702	115	A_{1g}
237	0	4	162	114	E_{2g}
200	4	0	10	0	A_{1g}
199	0	26	0	0	E_{1g}
196	0	0	69	44	E_{2g}
172	0	9	0	0	E_{1g}
161	0	6	130	111	E_{2g}
145	0	85	0	0	E_{1g}
138	111	14	9	0	A_{1g}
			Lattice Modes		
75	0	11	0	0	E_{1g}
55	0	0	25	15	E_{2g}
53	20	0	42	0	A_{1g}
45	0	7	0	0	
24	0	0	7	6	E_{2g}

[a] Peak heights recorded on an arbitrary scale and corrected for different scattering efficiencies of the crystal faces used.

$$2V = \Sigma K_r(\Delta r_i)^2 + \sum_i K_R(\Delta R_i)^2 + \sum_i H_\alpha(r_0\Delta\alpha_i)^2 + \sum_i H_\beta(r_0\Delta\beta_i)^2 + \sum_i H_\gamma(r_0\Delta\gamma_i)^2 + \sum_i H_\theta(r_0\Delta\theta_i)^2 + \sum_i F_a(\Delta a_i)^2 + \sum_i F_b(\Delta b_i)^2 + \sum_i F_c(\Delta c_i)^2 \qquad (3)$$

The general refinement procedure used has been previously described[22] but three further points should be noted: (1) mixing between the lattice and internal modes was not considered, (2) the frequencies of the E' modes were taken as the means of the E_{2g} and E_{1u} crystal mode frequencies, and (3) the frequency order of the symmetry species was maintained throughout the refinement process. Table V gives the refined set of force constants while Table VI shows the calculated frequencies together with the potential energy distribution between the force constants for each mode. The normal coordinates for all the vibrations in terms of the mass-weighted cartesian coordinates together with the corresponding symmetry coordinates for modes of "pure" bonding and stretching character are presented pictorially in Figures 4 and 5, respectively.

Table V. Refined Set of Force Constants (mdyn/Å) for the $Cr_2Cl_9{}^{3-}$ Ion

K_r	1.01	H_β	0.10	F_a	0.07
K_R	0.45	H_γ	0.12	F_b	0.09
H_α	0.14	H_θ	0.26	F_c	0.13

Discussion

Spectra. The vibrational data obtained from these single-crystal studies are in almost complete agreement with the group theoretical predictions based on the $D_{6h}{}^4$ space group. For each of the three complexes all but two of the crystal modes associated with the vibrations of the $Cr_2Cl_9{}^{3-}$ ion are observed. The E_{2g} component of ν_8 was observed as a very weak band only for $Cs_3Cr_2Cl_9$ and in none of the complexes could the E_{1u} component of ν_{11} be detected. In the lattice region both an E_{2g} and an E_{1u} mode were missing in all three complexes.

In addition to fundamentals, bands corresponding to overtone and combination modes were observed. The ordinary ray spectrum for each complex shows two strong reflection bands in the terminal Cr–Cl stretching region of which the higher frequency band was shown, by K–K analysis of the cesium complex, to be a weak oscillator. In effect, this weak band causes an inversion of the strong oscillator and the minimum observed between the two reflectance bands has been found to correspond closely to the true frequency of the weak band.[20,23] This low-intensity infrared band is assigned to a

Table VI. Observed and Calculated Frequencies (cm^{-1}) for the $Cr_2Cl_9{}^{3-}$ Ion and Potential Energy Contribution (%) of the Force Constants to Each Mode

	Calcd	Obsd[a]	K_r	K_R	H_α	H_β	H_γ	H_θ	F_a	F_b	F_c
A_1'	131	138	1	15	23	19	4	8	4	2	24
	206	200	32	10	21	4	4	48	19	0	3
	274	283	7	41	1	5	7	15	0	23	0
	368	378	43	4	12	0	12	25	1	1	1
A_2''	182	184	8	0	48	21	0	0	19	0	5
	243	256	23	21	0	6	20	0	3	0	26
	339	340	53	18	12	0	16	0	1	0	0
E′	80	75[b]	0	5	5	40	17	4	1	3	25
	159	161[b]	1	2	55	13	2	1	15	1	9
	206	193	14	3	0	30	26	2	0	5	20
	238	234	30	22	0	6	13	16	1	10	0
	358	352	46	20	3	15	0	14	0	1	1
E″	138	145	2	2	24	47	1	0	5	0	20
	170	172	18	23	27	12	6	0	11	0	2
	198	199	0	28	0	27	5	0	0	32	0
	330	337	71	11	4	10	2	0	0	0	2

[a] Frequencies taken from $Cs_3Cr_2Cl_9$ data. [b] Only one crystal component of E′ mode observed.

combination mode which, because of symmetry requirements,[24] could result from $\nu_4 + \nu_9$ ($A_{1g} + E_{1u}$), $\nu_7 + \nu_4$ ($A_{2u} + E_{1g}$), or $\nu_7 + \nu_{15}$ ($A_{2u} + E_{1g}$).

The Raman spectra of the A_{1g} modes for all complexes show a band of medium intensity on the low-frequency side of the strong band assigned to the terminal Cr–Cl stretching mode. Since only one A_{1g} stretching mode is predicted, the additional band is assigned to the first overtone of ν_7 (A_{2u}).[2] The frequency of ν_7 remains almost constant in these complexes while ν_1 increases by 15 cm^{-1} in going from cesium to potassium. Paralleling the increase in frequency of ν_1 there is a decrease in the intensity of the overtone band suggesting that the unusually high intensity is due to Fermi resonance with the A_{1g} stretching mode.

Grey and Smith[6] have attempted to relate structural changes in the $Mo_2Cl_9{}^{3-}$ ion to frequency variations in the infrared spectra. They concluded that the metal–halogen stretching frequencies are sensitive to structural changes of the $Mo_2Cl_9{}^{3-}$ ion and in particular compression or elongation of this anion caused by changes of the cation is reflected by the divergence or convergence of the bridging Mo–Cl stretching frequencies. Comparing the vibrational data for the chromium complexes there is certainly evidence for structural change; modes of predominantly stretching character increase in frequency on decreasing the cation size although, in general, the bending modes remain almost unchanged. This would indicate that there is a slight decrease in the Cr–Cl bond lengths from the cesium to the potassium complex. However in view of the extensive mixing between bridge stretching and bending modes, together with the possibility of mixing with the lattice modes, it is not felt that any useful information relating to changes in the shape of the $Cr_2Cl_9{}^{3-}$ ion can be derived from this spectral region. It may be, as suggested,[6] that the value of the A_2''–E' splitting in the terminal stretching region would give some estimation of the elongation of the anion but this is difficult to pursue since the correlation doublet for the E′ mode was only observed for the cesium complex.

In the lattice region the expected increase in frequency of nearly all modes on decreasing the mass of the cation was observed with the exception of the two E_{1g} modes for $K_3Cr_2Cl_9$. These occurred at considerably lower frequencies than the corresponding modes in the other two complexes and constituted the only difference in comparing both infrared and Raman spectral features. The validity of the symmetry assignments and frequencies of these lattice modes was confirmed by recording the E_{1g} spectra for all three complexes several times using *different* crystal samples and, even if complete crystallographic data for the potassium complex were available, it is difficult to explain this anomaly. From the X-ray structure of the cesium complex[14] it is found that there are two types of cation sites having the Wycoff notations (b) and (f). The (b) site cesium ions surround the anion and lie on the plane containing the bridging chlorine atoms while the remaining (f) site cations are located between the two anions in the unit cell on planes parallel and close to those of the terminal chlorine atoms. All the Cs–Cl bond distances are equal to within 0.1 Å. One of the E_{1g} lattice vibrations is a rotatory mode consisting of a slight torsional motion of the $Cr_2Cl_9{}^{3-}$ ion about the *x* and *y* axes and the frequency of this vibration together with that of the E_{1g} translatory mode will depend mainly on the relative position of the (f) site cations to the anion. It must be concluded, therefore, that the (f) cation–terminal chlorine bond distance in $K_3Cr_2Cl_9$ is greater than in the other two complexes thus causing a lowering in frequency of the E_{1g} lattice modes. The other lattice vibration which does not follow the normal trend on decreasing the cation mass is the A_{1g} translatory mode which remains at almost the same frequency for all three complexes indicating that it involves mainly a displacement of the $Cr_2Cl_9{}^{3-}$ ion.

Comparison of the infrared and Raman data published previously[8] with those of the present work shows reasonable agreement between the fundamental frequencies but differences as to the symmetry assignments of the observed bands. These differences are (1) in the terminal chromium–chlorine stretching region the frequency of A_{2u} mode was placed above that of the E_{1u} whereas the single-crystal study shows the reverse to be true and (2) as a result of assuming that the A_{1g} modes would have the strongest intensity in any group of bands[3,8] the previous workers indicated that bands observed in the Raman spectrum at about 160 and 140 cm^{-1} were A_{1g} and E_{2g}, respectively, but these should be assigned to E_{2g} and E_{1g} symmetries with the A_{1g} mode occurring as a weaker band at 138 cm^{-1}. In addition fundamentals observed in the region 130–100 cm^{-1} and the large number of overtones and combination and difference bands were not detected in the present study (with the exception of the two already mentioned).

Normal-Coordinate Analysis. Two points which immediately emerge from the force constant calculations are the importance of gaining prior knowledge as to the symmetry species of the fundamental modes of vibration and the danger of using a force field containing a large number of off-diagonal elements without some constraint being placed on their values. Using the symmetry assignments given by Ziegler and Risen[8] the UBFF would not refine and as far as could be determined no reasonable starting force field would result in the frequency of the A_{2u} terminal stretching mode occurring above that of the E_{1u} mode. The excellent agreement between the observed and calculated frequencies obtained by Ziegler and Risen[8] must be a function of the number of off-diagonal elements used in the force field. Although in the present work the agreement differs by as much as 12 cm^{-1}, symmetry relationships are maintained throughout the refinement process. This, in our view, is a physical constraint which must be placed upon the calculations.

The relative values of the force constants obtained, using the Urey–Bradley potential, are as expected with the terminal stretching approximately twice that of the bridge stretching force constant. The angle bending constants show no discernible trend which is not surprising since their values will, to a large extent, depend on those initially chosen for the interaction constants. Thus the relatively high value for H_θ is due to the fact that no Cr–Cr interaction constant is included. On being allowed to vary, the Cl–Cl interaction constants all increase from the values initially based on the Lennard-Jones 6–12 potential function which is to be expected since this function assumes the interaction of uncharged chlorine atoms. The charge on the chlorine atoms is clearly an important factor in this calculation since the values of the interaction constants are not related to the Cl–Cl bond distances. The largest interaction constant, F_c, is almost twice that of the Lennard-Jones value and suggests that there is a greater charge on the bridging than on the terminal chlorine atoms. This result is of interest since it lends some support to the proposed description[15] of $Cs_3Cr_2Br_9$ as consisting of pyramidal $CrBr_3$ units separated by layers of Br^- ions.

The form of the normal modes of vibration is most easily described for the nondegenerate A_1' and A_2' symmetry species. With the exception of the lowest frequency A_1' vibration, which involves a breathing motion of the bridging framework, modes which consist largely of $(Cr–Cl)_t$ stretching and bending and $(Cr–Cl)_b$ stretching are observed although some mixing between them does occur. For example the A_1' mode at 274 cm^{-1}, while predominantly a $(Cr–Cl)_b$ stretching vibration, does involve some $(Cr–Cl)_t$ stretching character.

Of the E' and E'' modes, those at 358 and 330 cm^{-1} are almost pure $(Cr–Cl)_t$ stretching vibrations. However, because of symmetry requirements for these doubly degenerate modes, vibrations involving the bridging framework will consist of both bending and stretching motions and this results in a group of vibrations having a mixture of these characteristics together with $(Cr–Cl)_t$ bending. The vibration of highest frequency in this group, the E' mode at 238 cm^{-1}, clearly involves the greatest amount of $(Cr–Cl)_b$ stretching and is thus isolated from the other bands which range from 206 to 159 cm^{-1}.

In the remaining two degenerate modes, a wagging motion of the $CrCl_3$ group predominates although in practice the E' mode at 80 cm^{-1} will have a large degree of lattice character. In fact this mixing of lattice modes is likely to occur with other low-frequency internal modes but, because the frequency separation is in the order of 70 cm^{-1}, it is expected to be small.

One major point of difference between our calculations and those of Ziegler and Risen is the assignment of the breathing mode of A_1' symmetry and since this mode will, for the $W_2Cl_9^{3-}$ ion, involve stretching of the W–W bond, further comment is appropriate. In the earlier calculation this breathing mode was placed at higher frequency (161 cm^{-1}) than the $(Cr–Cl)_t$ bend of A_1' symmetry (121 cm^{-1}) which is the reverse of the present assignment where the breathing mode and the $(Cr–Cl)_t$ bend are observed at 138 and 200 cm^{-1}, respectively. However, the appearance of the $(Cr–Cl)_t$ bend of A_2'' symmetry at 184 cm^{-1} makes the calculated frequency of 121 cm^{-1} seem unreasonably low. Further evidence for the present assignment comes from Raman intensity measurements. In the $x(zz)y$ scattering orientation the band at 138 cm^{-1} is considerably stronger than that at 200 cm^{-1} in keeping with the concept that there will be a greater change in polarizability for the breathing vibration than for the $(Cr–Cl)_t$ bend. In $K_3W_2Cl_9$ the band at 139 cm^{-1} is assigned to the breathing mode of A_1' symmetry and in view of the relatively high Raman intensity observed for this band it is likely that the assignment is correct. One of the key steps in Ziegler and Risen's calculations of k_{W-W} is the transference, from $Cs_3Cr_2Cl_9$, of those force constants relating to deformation of the bridging framework. Since it now appears that these constants have been overestimated, due to the breathing mode of A_1' symmetry in $Cs_3Cr_2Cl_9$ being wrongly assigned, then the calculated value of k_{W-W} will be low. However, since unambiguous symmetry assignments for the $W_2Cl_9^{3-}$ were unavailable, we did not repeat this calculation.

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Registry No. $K_3Cr_2Cl_9$, 24387-17-5; $Rb_3Cr_2Cl_9$, 24354-96-9; $Cs_3Cr_2Cl_9$, 21007-54-5.

Supplementary Material Available. Figures 4 and 5 giving the pictorial forms of the normal and symmetry coordinates in terms of the mass-weighted cartesian coordinates and Table VII listing the cartesian symmetry coordinates 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 the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.00 for photocopy or $2.50 for microfiche, referring to code number AIC406230.

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