# Preparation and Vibrational Spectra of the $MX_6{}^{2-}$ and $MX_4Y_2{}^{2-}$ Ions (M = Ti or Sn; X = Cl, Br, or I)

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The infrared and Raman spectra of tetraethylammonium complexes of the $TiCl_6{}^{2-}$ and $TiBr_6{}^{2-}$ ions have been recorded in the range 70–1000 cm⁻¹. The new Raman spectra of the $TiCl_6{}^{2-}$ ion are in complete disagreement with the previous study and are much more reasonable in comparison with the spectra of the analogous $SnX_6{}^{2-}$ ions, which are also included. The data for the $TiBr_6{}^{2-}$ ions are reported for the first time. The following mixed-halo species of the type $MX_4Y_2{}^{2-}$ have been prepared as tetraethylammonium salts: $TiCl_4Br_2{}^{2-}$, $TiCl_4I_2{}^{2-}$, $TiCl_2Br_4{}^{2-}$, $SnCl_4Br_2{}^{2-}$, $SnCl_4I_2{}^{2-}$, $SnCl_2Br_4{}^{2-}$, $SnCl_2I_4{}^{2-}$, $SnBr_4I_2{}^{2-}$, and $SnBr_2I_4{}^{2-}$. The infrared spectra of all of these salts have been recorded, as well as the Raman spectra of the first seven; the remaining two salts, as well as $[(C_2H_5)_4N]_2SnI_6$, decomposed immediately in the laser beam. It is concluded from a study of these vibrational spectra that most and possibly all of the mixed anions possess the *cis* configuration in the solid state.

## Introduction

In 1936, Rumpf[1] recorded the Raman spectrum of titanium tetrachloride in concentrated hydrochloric acid, reporting three bands at 463, 340, and 252 cm⁻¹; she concluded that the $TiCl_6{}^{2-}$ ion was the absorbing species. Subsequently, Kohlrausch assigned the bands, respectively, to the $\nu_1(a_{1g})$, $\nu_2(e_g)$, and $\nu_5(t_{2g})$ vibrational modes of the complex ion. Yet by comparison with the spectra of other $MCl_6{}^{2-}$ ions, notably those of germanium, tin, and lead for which $\nu_1 - \nu_3 \sim 20$ cm⁻¹, these assignments seem to be incorrect. In particular, the reported value of $\nu_1$ at 463 cm⁻¹ is over 100 cm⁻¹ above the value which might have been predicted by comparison with that of the $SnCl_6{}^{2-}$ ion. Accordingly, we have reinvestigated the Raman spectrum of the $TiCl_6{}^{2-}$ ion, and found that it bears no similarity to the original spectrum. We have also obtained (for the first time) the corresponding data for the $TiBr_6{}^{2-}$ ion. Complete infrared spectra on these ions are reported. The spectra of the analogous tin salts were also recorded for comparative purposes.

In addition, as many mixed halo species as possible of the type $MX_4Y_2{}^{2-}$ have been prepared and their vibrational spectra studied in order to determine whether the complex ions adopt the *cis* or the *trans* configuration in the solid state.

## Experimental Section

**Preparation of Compounds.**—The titanium salts were prepared by adding a solution of the titanium halide in dichloromethane to an excess of the appropriate tetraethylammonium halide in the same solvent. The complexes, which precipitated immediately, were filtered off onto a sintered-glass disk under dry nitrogen and then washed at least three times with dichloromethane. The complexes were then dried under vacuum and sealed into glass manifolds. The $TiX_6{}^{2-}$ ions are well established[2] where X = Cl or Br but not where X = I; the $TiCl_4Br_2{}^{2-}$ ion has been prepared once previously,[3] but the $TiCl_2Br_4{}^{2-}$ and $TiCl_4I_2{}^{2-}$ ions are reported for the first time. All preparations must be carried out using rigorously dried solvents on a vacuum line. The analytical data are given in Table I.

The tin salts were prepared by mixing ethanol solutions of the appropriate reagents; the compounds precipitated immediately and were filtered off, washed with ethanol, and dried. The ammonium salts of the $SnBr_4Cl_2{}^{2-}$ and $SnCl_4I_2{}^{2-}$ ions[4] have been referred to previously but have not been adequately characterized; the remaining mixed-halo salts appear to be new compounds.

**Infrared Spectra.**—The infrared spectra of the complexes were recorded on the following instruments: Perkin-Elmer 337 (1300–400 cm⁻¹), Grubb-Parsons DM2 (455–200 cm⁻¹), and GM 3 (200–70 cm⁻¹). The Nujol mulls were prepared in a drybox where appropriate. The instruments were calibrated against the spectrum of water vapor.[5] The low solubility of the salts in suitable solvents precluded their study in solution in most cases. Data below 200 cm⁻¹ were obtained at liquid nitrogen temperature.

**Raman Spectra.**—The spectra were recorded on a Cary 81 spectrometer using a He–Ne laser source (6328 Å). The titanium samples were wax-sealed into flat-bottomed glass containers and held in such a way that the laser beam was normal to the flat surface. The tin samples, which are stable in moist air, were held in the standard metal cone supplied with the instrument. The complexes were all in the form of powdered solids.

## Results and Discussion

**$MX_6{}^{2-}$ Ion Spectra.**—Regular octahedral molecules give rise to six normal modes of vibration; of these, $\nu_1(a_{1g})$, $\nu_2(e_g)$, and $\nu_5(t_{2g})$ are Raman active, $\nu_3(t_{1u})$ and $\nu_4(t_{1u})$ are infrared active, and $\nu_6(t_{2u})$ is inactive. The assignments of the observed bands are generally obvious and comparable with those of related hexahalo species.[6] They are given in Table II.

The most important result is that $\nu_1$ for the $TiCl_6{}^{2-}$ ion occurs as a very strong band in the Raman spectrum at 320 cm⁻¹, *i.e.*, 143 cm⁻¹ below the previously reported value. Moreover, neither $\nu_2$ nor $\nu_5$ agrees with the previous data, and it is clear that Rumpf[1] must have been studying in solution a species different from the $TiCl_6{}^{2-}$ ion, probably a hydrolysis product derived therefrom. In nitromethane solution, $\nu_1$ occurs as a very strong polarized band at 319 cm⁻¹, $\nu_2$ occurs at

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Table I

Analytical Data and Colors

| Complex | Color | % C Calcd | % C Found | % H Calcd | % H Found | % N Calcd | % N Found |
|---|---|---|---|---|---|---|---|
| [(C$_2$H$_5$)$_4$N]$_2$TiCl$_6$ | Yellow | 36.9 | 37.2 | 7.7 | 7.7 | 5.4 | 5.5 |
| [(C$_2$H$_5$)$_4$N]$_2$TiBr$_6$ | Red | 24.4 | 23.8 | 5.1 | 4.9 | 3.5 | 3.2 |
| [(C$_2$H$_5$)$_4$N]$_2$TiCl$_4$Br$_2$ | Yellow-orange | 31.5 | 31.1 | 6.6 | 6.6 | 4.6 | 4.5 |
| [(C$_2$H$_5$)$_4$N]$_2$TiCl$_4$I$_2$ | Brown-black | 27.3 | 27.5 | 5.7 | 5.7 | 4.0 | 3.7 |
| [(C$_2$H$_5$)$_4$N]$_2$TiCl$_2$Br$_4$ | Orange-red | 27.5 | 28.2 | 5.8 | 5.9 | 4.0 | 4.1 |
| [(C$_2$H$_5$)$_4$N]$_2$SnCl$_6$ | White | 32.5 | 31.6 | 6.8 | 6.5 | 4.7 | 4.8 |
| [(C$_2$H$_5$)$_4$N]$_2$SnBr$_6$ | Yellow | 22.4 | 22.3 | 4.7 | 4.6 | 3.3 | 3.4 |
| [(C$_2$H$_5$)$_4$N]$_2$SnI$_6$ | Very dark red | 17.4 | 18.0 | 3.6 | 3.7 | 2.5 | 2.7 |
| [(C$_2$H$_5$)$_4$N]$_2$SnCl$_4$Br$_2$ | White | 28.2 | 27.7 | 5.9 | 5.8 | 4.1 | 3.7 |
| [(C$_2$H$_5$)$_4$N]$_2$SnCl$_4$I$_2$ | Orange | 24.8 | 24.8 | 5.2 | 5.1 | 3.6 | 3.7 |
| [(C$_2$H$_5$)$_4$N]$_2$SnCl$_2$Br$_4$ | Pale yellow | 25.0 | 25.0 | 5.2 | 5.2 | 3.6 | 3.5 |
| [(C$_2$H$_5$)$_4$N]$_2$SnCl$_2$I$_4$ | Dark red | 20.1 | 19.5 | 4.2 | 4.0 | 2.9 | 2.6 |
| [(C$_2$H$_5$)$_4$N]$_2$SnBr$_4$I$_2$ | Red-brown | 20.2 | 20.4 | 4.2 | 4.2 | 2.9 | 2.8 |
| [(C$_2$H$_5$)$_4$N]$_2$SnBr$_2$I$_4$ | Dark red | 18.4 | 18.7 | 3.9 | 3.9 | 2.7 | 2.6 |

Table II

Vibrational Spectra (cm$^{-1}$) of the Tetraethylammonium Salts of the MX$_6^{2-}$ Ions (M = Ti or Sn; X = Cl, Br, or I)$^a$

| | $\nu_1(a_{1g})$ | $\nu_2(e_g)$ | $\nu_3(t_{1u})$ | $\nu_4(t_{1u})$ | $\nu_5(t_{2g})$ |
|---|---|---|---|---|---|
| TiCl$_6^{2-}$ | 320 vs | 271 vw | 316 s, asym | 183 s | 173 s |
| TiBr$_6^{2-c}$ | 192 vs | ... | 244 vs | 119 m | 115 vw, sh |
| SnCl$_6^{2-}$ | 309 vs | 232 w | 291 s$^b$ | 163 s | 159 vs |
| SnBr$_6^{2-}$ | 182 vs | 135 m | 203 vs | 111 m | 101 s |
| SnI$_6^{2-}$ | $d$ | $d$ | 156 s | 90 sh, 79 m | $d$ |

$^a$ All refer to the solid state. $^b$ Shoulder at 306 cm$^{-1}$. $^c$ A weak band at 88 cm$^{-1}$ may be $\nu_6(t_{2u})$, which is strictly inactive in O$_h$ symmetry. $^d$ Decomposed in laser beam.

Table III

Species of the Vibrational Modes$^a$ of Ions of the Type MX$_4$Y$_2^{2-}$

| | Symmetry point group | $\nu$(MX) | $\nu$(MY) | Skeletal bending modes |
|---|---|---|---|---|
| cis-MX$_4$Y$_2^{2-}$ | C$_{2v}$ | 2a$_1$ + b$_1$ + b$_2$ | a$_1$ + b$_1$ | 3a$_1$ + 2a$_2$ + 2b$_1$ + 2b$_2$ |
| trans-MX$_4$Y$_2^{2-}$ | D$_{4h}$ | a$_{1g}$ + b$_{1g}$ + e$_u$ | a$_{1g}$ + a$_{2u}$ | b$_{2g}$ + e$_g$ + a$_{2u}$ + b$_{2u}$ + 2e$_u$ |

$^a$ Vibrational species which are underlined are infrared active; all species are Raman active in C$_{2v}$, but in D$_{4h}$ only those which are infrared inactive are Raman active.

$\nu_3$ decreases with increase in the size of the cation as follows: K$^+$ > Rb$^+$ > Cs$^+$ > (C$_2$H$_5$)$_2$NH$_2^+$ > (C$_2$H$_5$)$_4$N$^+$.

The asymmetric bending mode, $\nu_4$, for this ion has been observed once previously,[10] for the cesium salt, at 190 cm$^{-1}$; i.e., $\nu_4$ also falls in the order Cs$^+$ > (C$_2$H$_5$)$_4$N$^-$ (cf. ref 8 a similar observation on MF$_6^{2-}$ ions).

Apart from a single report[9] of $\nu_3$ for the diethylamino salt, the vibrational spectrum of the TiBr$_6^{2-}$ ion is reported here for the first time. One mode, $\nu_2$, was too weak to be observed in the Raman spectrum. The mode $\nu_1$, apart from appearing as a very strong band in the Raman spectrum, also occurred weakly in the infrared spectrum. This fact indicates that the O$_h$ selection rules have been relaxed and that the complex ion is on a low-symmetry site in the lattice.

The vibrational spectra of the SnCl$_6^{2-}$ and SnBr$_6^{2-}$ ions have been recorded previously[11] (see ref 6 for a summary). However, it was considered important to gather the complete vibrational spectra of these ions as the tetraethylammonium salts in order to obtain the closest comparison with the spectra of the analogous titanium salts. Only the infrared spectra of the SnI$_6^{2-}$ ion could be obtained, owing to the immediate decom-

275 cm.$^{-1}$, and $\nu_5$ is too weak to be observed. The order of the intensities in solution ($\nu_1 > \nu_2 > \nu_5$) is thus different from that in the solid state ($\nu_1 > \nu_5 > \nu_2$) (Figure 1). The asymmetric stretching mode, $\nu_3$, for
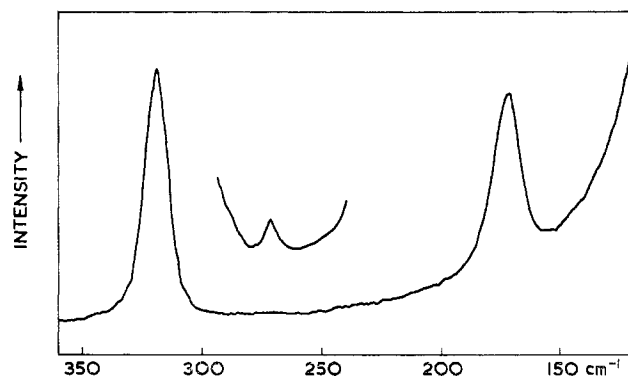


Figure 1.—Raman spectrum of [(C$_2$H$_5$)$_4$N]$_2$TiCl$_6$ in the solid state; inset shows $\nu_2$ at the maximum sensitivity of the instrument.

the TiCl$_6^{2-}$ ion has been observed previously;[7–9] coupled with the present results, the combined data indicate that

position of this salt in the laser beam. The effect of increase in the size of the cation is to decrease the stretching frequencies of the anion, as noted above for the TiCl$_6^{2-}$ ions and previously[12] for the NbX$_6^{n-}$ and TaX$_6^{n-}$ ions.

The one previous measurement of the infrared spectrum of the SnI$_6^{2-}$ ion, as the cesium salt,[13] places $\nu_3$ at 165 cm$^{-1}$ consistent with the present measurement (156 cm$^{-1}$, i.e., Cs$^+$ > (C$_2$H$_5$)$_4$N$^+$). However in the spectrum of this salt in the bending frequency region, two bands were observed; the first, at 86 cm$^{-1}$, was assigned as a translational lattice mode of t$_{1u}$ symmetry, whereas the second, at 48 cm$^{-1}$, was assigned as $\nu_4$. We consider that these assignments should be reversed, because the band near 90 cm$^{-1}$ is almost independent of the mass of the cation, whereas a lattice mode should be strongly dependent thereon. Moreover, for all other MX$_6^{2-}$ salts, $\nu_4$ demonstrably lies above the lattice mode. We also point out that the assignments for $\nu_4$ and $\nu$(lattice) for the SnBr$_6^{2-}$ salts, as given in ref 13, should be reversed for the same reasons.

MX$_4$Y$_2^{2-}$ Ions.—The vibrational spectra of the

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TABLE IV

VIBRATIONAL SPECTRA OF THE $MX_4Y_2^{2-}$ IONS $(CM^{-1})$

| Ion | Type[b] of spectrum | $\nu(MCl)$ | $\nu(MBr)$ | $\nu(MI)$ | Skeletal bending modes |
|---|---|---|---|---|---|
| $SnCl_4Br_2^{2-}$ | R | 304 vs, 287 w, 264 m, 254 mw | 204 s, 180 m, br | | 157 m, 144 w, sh |
| | ir | 306 sh, 290 vs, 267 s, 252 m | 204 m, 184 m | | 172 m, 160 s, 149 m, 129 w |
| $SnCl_4I_2^{2-}$ | R | 293 m, 273 s | | 159 w, sh | ∼177 w, 110 w |
| | ir | 296 vs, 278 s, 254 m | | 160 s, br | 143 w |
| $SnCl_2Br_4^{2-}$ | R | 298 s, 288 sh, 260 m | 200 vs, 187 s | | ∼153 vw, sh |
| | ir | 292 s, 276 s | 202 vs, 184 vw | | 164 w, 155 m, 147 s, 128 w, 113 w |
| $SnCl_2I_4^{2-}$ | R | a | | | |
| | ir | 304 s, 261 m | | 160 s, br | |
| $SnBr_4I_2^{2-}$ | R | a | | | |
| | ir | | 197 s, 189 sh | 166 m | |
| $SnBr_2I_4^{2-}$ | R | a | | | |
| | ir | | 195 sh, 186 s | 162 s | 110 w, 101 w, 94 w |
| $TiCl_4Br_2^{2-}$ | R | 316 s, 300 m | 212 s | | 204 m, 180 w |
| | ir | 344 sh, 312 vs, br, 283 m | 240 m | | 196 m, 185 s, 178 s |
| $TiCl_2Br_4^{2-}$ | R | 318 m | 214 m | | 195 s, 183 m |
| | ir | 344 m, 313 vs, asym | 240 vs | | 196 m, 185 ms, 178 s, 152 w? |
| $TiCl_4I_2^{2-}$ | R | c | | | |
| | ir | 331 vs, 280 s | | 192 vs ? | 213 m, 200 s, 176 m, 166 m |

$^a$ Compound decomposes in laser beam.   $^b$ R, Raman active; ir, infrared active.   $^c$ Unsatisfactory Raman spectrum.

$MX_4Y_2^{2-}$ ions have been studied in order to ascertain whether the ions crystallize in the *cis* or *trans* configurations. In the former case, the anions would have $C_{2v}$ symmetry, whereas in the latter, they would be centrosymmetric with $D_{4h}$ symmetry. The symmetries of the normal modes for the two possible configurations are given in Table III. There should be no coincidences between the infrared and Raman bands for ions with the *trans* configuration.

For ions with the *cis* configuration, however, all modes are Raman active, and all but the $a_2$ modes are infrared active. In this case there should therefore be 13 coincidences, four of which correspond to essentially MX stretches, two to essentially MY stretches, and the remaining seven to skeletal bending modes. The data reported in the previous section help to define the regions over which the different MX stretching frequencies would be expected to occur.

The data are given in Table IV. In general, bands are less well resolved below 200 cm$^{-1}$, both in the infrared and in the Raman spectra, and so any structural conclusions are best based on the MX stretching frequencies. The appearance of several well-resolved bands in the SnCl stretching frequency region (four in the case of the $SnCl_4Br_2^{2-}$ ion) attests to the conclusion that all the tin–chloro anions, $SnCl_4Br_2^{2-}$, $SnCl_4I_2^{2-}$, $SnCl_2Br_4^{2-}$, and $SnCl_2I_4^{2-}$, have the *cis* configuration in the solid state. While some crystal field splitting of the bands cannot be excluded, this is seldom sufficient in the case of the $MX_6^{2-}$ ions (Table II), and with the present instruments, to be resolvable. Thus the structural conclusion is considered to be valid despite the fact that only solid-state spectra are involved. Moreover, the pattern of the SnCl stretching modes in the $SnCl_4X_2^{2-}$ ions is similar to that in $SnCl_4$·bipy, for which only the *cis*-octahedral structure is possible.[14] Solution spectra on the mixed-halo complexes were not

possible, either because of insufficient solubility of the complexes (in most solvents) or because of disruption of the complexes (in $CH_3NO_2$, $CH_3CN$, $C_5H_5N$, or $H_2O$). The bromoiodo anions, $SnBr_4I_2^{2-}$ and $SnI_4Br_2^{2-}$, decomposed in the laser beam and also gave less well-resolved infrared spectra than did the chloro anions. Consequently, no definite statement regarding their stereochemistry can be made.

The titanium complexes are strongly colored, especially those which contain bromide. Consequently, their Raman spectra are weaker than those of tin. In the TiCl stretching frequency region, the $TiCl_4Br_2^{2-}$ ion apparently contains two Raman-active bands and three infrared-active bands, whereas in the TiBr stretching frequency region, there is one of each kind. The infrared-active band centered at 312 cm$^{-1}$ is very broad and asymmetric; in view of this and of the close proximity of $\nu_1$ to $\nu_3$ for the $TiCl_6^{2-}$ ion, the band is likely to be the envelope of several infrared-active modes. This line of reasoning suggests the *cis* configuration. Although we cannot reach an unequivocal conclusion regarding the stereochemistry of this ion or of the $TiCl_2Br_4^{2-}$ ion, our opinion is that they have the *cis* configuration.

### Conclusion

The evident preponderance and possible universality of the *cis* configuration for the present complexes suggest that the $\pi$-donor ability of the halogens to the $t_{2g}$ orbitals of the metal is the major factor favoring this configuration over the sterically more favorable *trans* configuration. In the latter situation the better $\pi$-electron donors (bromide or iodide, depending upon the anion) would be competing for the same $t_{2g}$ orbital, whereas in *cis* complexes, they could $\pi$-donate into different $t_{2g}$ orbitals; the *cis* complexes should thus be more stable. A similar argument has been used previously by Jaffé[15] and more recently by Bradley and

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Holloway[16] to rationalize the greater stability of *cis*-dialkoxybis(acetylacetonato)titanium(IV) complexes relative to the *trans* isomers.

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# Magnetic and Spectroscopic Studies of Salts of M₂X₉³⁻

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Preparative procedures for certain enneahalodimetalates (M₂X₉³⁻), containing first-row transition metal ions, are reported. Many of these had been previously mentioned in the literature, but details in their preparation were lacking. The new compounds Cs₃Cr₂X₉ (X = Br or I) are described. All alkali metal salts appear to be isomorphous. The temperature dependence of their paramagnetic suscepibility has been measured between 80 and 300°K. It is shown that magnetic dilution with salts of Cr₂Cl₉³⁻ is attained only with alkylammonium cations. The small, positive susceptibility of Cs₃W₂Cl₉ has been attributed to temperature-independent paramagnetism. Single-crystal spectra of Cs₃M₂Cl₉ (M = Ti, Cr, and V) are reported and interpreted in terms of transitions which are essentially localized on adjacent metal atoms, in contrast to the transitions in W₂Cl₉³⁻ which are believed to be due to delocalized electrons. A further sharp contrast is provided in the reactions of Cr₂Cl₉³⁻ and W₂Cl₉³⁻ with pyridine.

The enneahalodimetalates are an interesting but small class of compounds which can simultaneously embody a general structural similarity and a significant structural difference. The structures of Cs₃Cr₂Cl₉ and K₃W₂Cl₉ have been fully characterized by X-ray analyses.[1,2] In both, the anion can be described as two octahedra sharing a common trigonal face. However, considerable differences in detail are present in the two structures. The chromium atoms in Cr₂Cl₉³⁻ do not lie exactly at the centers of their respective octahedra but are displaced away from each other along the trigonal axis, so that their interatomic distance is 3.1 Å. On the other hand, this phenomenon is exactly reversed in K₃W₂Cl₉. The metal atoms are displaced toward each other causing the shared face to be somewhat larger than those on the periphery. The interatomic separation of the metal atoms is only 2.4 Å. Cotton[3] has presented a clear and convincing criterion for metal–metal bonding in general and in particular for its presence in W₂Cl₉³⁻ and its absence in Cr₂Cl₉³⁻. Since there appears to be a force operating between the tungsten atoms such that the metal atoms approach one another more closely than the bridging geometry would appear to require, metal–metal bonds are likely to exist in W₂Cl₉³⁻. Conversely in Cr₂Cl₉³⁻, the structure indicated a net repulsion and the lack of any major metal–metal interaction. Magnetic data obtained at room temperature are believed to reflect these properties. It is often claimed that K₃W₂Cl₉ is diamagnetic; however, Klemm and Steinberg[4] actually found a small, positive susceptibility corresponding to a magnetic mo-

ment of 0.47 BM. On the other hand, the magnetic moment[1] of Cs₃Cr₂Cl₉ has been reported as 3.82 BM per chromium atom. The magnitude of the spin interaction, if any, was not determined. However, a study of the temperature dependence of the magnetic susceptibility[5] of [(CH₃CH₂)₄N]₃Cr₂Cl₉ has indicated that the exchange constant is only −5°K or 0.01 kcal/mol, an insignificant quantity in terms of chemical bonding. It should be noted that the magnetic moment of 3.96 BM at room temperature reflects a considerable difference in the paramagnetic susceptibility when compared to that obtained for Cs₃Cr₂Cl₉.

While Cs₃Tl₂Cl₉ is well known,[6] other examples of compounds of similar stoichiometry, but containing paramagnetic metal atoms, are not plentiful. The existence of K₃M₂Cl₉ (M = Nd or Pr) has been indicated in a phase study,[7] but only Cs₃M₂Cl₉ (M = Ti or V) and Cs₃Ti₂Br₉ have been isolated.[1,8] Each of these are isomorphous with Cs₃Cr₂Cl₉, but no detailed structural or magnetic information was presented. However, the similarity of the lattice constants suggests that the interatomic separation of the metal atoms is also about 3.1–3.2 Å in each case, so that metal–metal bonding would not exist according to Cotton.

It is remarkable that general preparative methods for the enneahalodimetalates which contain first-row transition metal atoms have not been reported in detail. Furthermore, with the exception of [(CH₃CH₂)₄N]₃Cr₂Cl₉, data pertaining to their temperature-dependent paramagnetism have not been available. Initially, we obtained these data for Cs₃Cr₂Cl₉, and the wide dis-

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