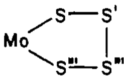
Table V. Dimensions (Å, deg) within Molybdenum Tetrasulfide Moieties



	$[AsPh_4]_2[Mo_2S_{10}]\cdot 0.5MeCN$[c]		$[(\eta^5\text{-}C_5H_5)_2\text{-}MoS_4]$[d]
	a	*b*	
Mo–S	2.409 (2)		2.455
Mo–S'''	2.403 (3)		2.451
S–S'	2.019 (5)	2.169 (14)	2.085
S'''–S''	2.115 (5)	2.096 (16)	2.081
S'–S''	1.970 (6)	1.936 (19)	2.018
S–Mo–S'''	85.1 (1)		88.2
Mo–S–S'	105.0 (1)	100.3 (5)	108.4
Mo–S'''–S''	110.5 (2)	104.0 (4)	108.8
S–S'–S''	92.1 (3)	109.7 (8)	99.9
S'''–S''–S'	102.1 (2)	81.5 (9)	100.8
dist from MoS'S''' plane S'	1.322 (5)	0.377 (18)	−0.65
dist from MoS'S''' plane S''	0.312 (5)	1.615 (16)	0.53

[a] Major component of disorder. [b] Minor component of disorder. [c] This work. [d] Reference 29.

interbond angles is observed. The dimensions of these tetrasulfido groups are listed in Table V, which contains a comparison with the corresponding details for $[(\eta^5\text{-}C_5H_5)_2MoS_4]$.[29] The conformation of the tetrasulfido group characterized here differs from that identified for $[(\eta^5\text{-}C_5H_5)_2MoS_4]$ and its tungsten analogue.[38] Thus, for $[(\eta^5\text{-}C_5H_5)_2MoS_4]$, the central sulfur atoms lie at approximately equal distances (0.53 and 0.65 Å) from, and on opposite sides of, the plane containing the molybdenum and two coordinated sulfur atoms. Nevertheless, the pattern that the central S–S bond is shorter than the other two S–S bonds is also manifest for both of these $[(\eta^5\text{-}C_5H_5)_2MoS_4]$ molecules, albeit to a smaller extent than in $[Mo_2S_{10}]^{2-}$.

The mechanism for the formation of $[Mo_2S_{10}]^{2-}$, from the reaction between $[Mo_2S_{12}]^{2-}$ and PhSNa (1:16) described in the Experimental Section, presumably involves the abstraction by the benzenethiolate of sulfur atoms from some of the persulfido groups of the initial complex, with some subsequent insertion of two sulfur atoms into one of the remaining terminal persulfido groups. However, why the particular complex should be formed is not clear.

Conclusions

The complex $[Mo_2S_{10}]^{2-}$, which contains terminal sulfido, bridging sulfido, persulfido, and tetrasulfido groups has been isolated and characterized by X-ray crystallography; the respective Mo–S bond lengths are 2.110 (2), 2.32 (2), 2.395 (3), and 2.406 (3) Å.

Acknowledgment. We thank the Verband der Chemischen Industrie (W.C. and G.M.S.) and the Science Research Council (G.C. and C.D.G.) for financial support.

Registry No. $[AsPh_4]_2[Mo_2S_{10}]\cdot 0.5MeCN$, 76550-05-5; $[NH_4]_2[Mo_2S_{12}]$, 68417-00-5.

Supplementary Material Available: Tables of thermal parameters and structure factors (43 pages). Ordering information is given on any current masthead page.

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Crystal Structure and Low-Temperature Crystal Spectra of Dicesium Dichlorotetraaquochromium(III) Chloride

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$Cs_2CrCl_5\cdot 4H_2O$ has been found by X-ray diffraction to belong to the monoclinic space group $C2/m$ with $a = 17.604$ Å, $b = 6.140$ Å, $c = 6.979$ Å, $\beta = 106.04°$, and $Z = 2$. The compound contains *trans*-$[CrCl_2(H_2O)_4]^+$ groups. The principal bond lengths are as follows: Cr–Cl, 2.302; Cr–O, 1.925; O–H···Cl, 3.006 and 3.062 Å. The latter values indicate strong hydrogen bonding in the crystal. The bands at 16.63, 21.76, 23.04, and 35.13×10^3 cm^{-1} in the polarized crystal spectra have been assigned to spin-allowed transitions. Since the chromophore has almost exact D_{4h} symmetry, selection rules of this group have been used to label the transitions. The decrease of the band areas on cooling indicates that vibronic coupling is the principal source of band intensity. Two extensive sets of sharp, weak bands starting at 14.43×10^3 and 20.69×10^3 cm^{-1} are assigned as spin-forbidden transitions to states originating from octahedral $^2E_g + {}^2T_{1g}$ and $^2T_{2g}$, respectively. A σ-polarized band at 19.70×10^3 cm^{-1} is due to coupling of ν(O–H) to a component of the lowest spin-allowed band; upon deuteration of the compound the band shifts to lower energy by the expected amount. An iron(III) impurity causes the appearance of bands at 28.18×10^3 cm^{-1} (π) and 31.01×10^3 cm^{-1} (σ). The former is most probably a Cl → Fe charge-transfer band of the *trans*-$[FeCl_2(H_2O)_4]^+$ group; the latter has not been assigned.

Introduction

A large number of halo–aquo complexes of the first-row transition metals are known, and the crystal structures of many have been determined by X-ray diffraction.[2] A significant number of these contain the *trans*-$[MX_2(H_2O)_4]^{n+}$ chromophore, among which are $CrCl_3\cdot 6H_2O$ (green isomer),[3] $MCl_3\cdot 6H_2O$ (M = Ti, V, Fe),[4] $VBr_3\cdot 6H_2O$,[4] $CoCl_2\cdot 6H_2O$,[5] $NiCl_2\cdot 6H_2O$,[6] and $FeCl_2\cdot 4H_2O$.[7] Although these compounds show varying degrees of deviation from tetragonal symmetry, they provide a rather extensive series of chromophores of approximate D_{4h} symmetry. In cases where single crystals of

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(1) (a) Canisius College. (b) Medical Foundation of Buffalo.

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0020-1669/81/1320-1566$01.25/0

Table I. Fractional Coordinates and Anisotropic Thermal Parameters ($\times 10^4$) for $Cs_2CrCl_5 \cdot 4H_2O$ (Esd's in Parentheses)[a]

atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cs	0.2978	0	0.2514 (1)	20	185 (2)	96 (1)	0	22 (1)	0
Cr	0	0	0	11	71 (4)	81 (4)	0	27 (2)	0
Cl(1)	0.3066 (1)	0	0.7563 (4)	16 (1)	170 (6)	123 (5)	0	36 (3)	0
Cl(2)	0.3931 (1)	$^1/_2$	0.1294 (4)	15	152 (6)	140 (4)	0	55 (2)	0
Cl(3)	0	$^1/_2$	$^1/_2$	21 (1)	181 (9)	101 (6)	0	49 (4)	0
O	0.0484 (5)	0.2222 (19)	0.1888 (14)	96 (2)	1397 (32)	917 (18)	−656 (14)	545 (8)	−2113 (36)

[a] The form of the anisotropic temperature factor is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

adequate size can be prepared, they can be used to study the effect of low-symmetry ligand fields on the absorption spectra of the complexes in the solid state. This is most instructive if low-temperature as well as room-temperature spectra are recorded with the use of polarized light.

The low-temperature crystal spectra of $CoCl_2 \cdot 6H_2O$ have ben recorded in detail by Ferguson and Wood.[8] Few spectral studies of comparable depth have been reported for the other halo–aquo complexes of the first-row transition metals. Their study is particularly interesting in that the spectra contain anomalous bands which can be assigned to the coupling of the O–H stretching vibration of water to the ligand field bands. As we shall show, the same phenomenon is observed in the spectra of the compounds under study in this paper and the following one.[9]

Green $CrCl_3 \cdot 6H_2O$ has been shown by X-ray diffraction to contain the *trans*-$[CrCl_2(H_2O)_4]^+$ chromophore.[3] This compound is, however, ill-suited for crystal spectroscopy since it is hygroscopic and its crystals are fragile and almost always multiple. In this paper, we present the preparation, structure, and ligand field spectra of the very stable $Cs_2CrCl_5 \cdot 4H_2O$, which also contains the *trans*-$[CrCl_2(H_2O)_4]^+$ chromophore. In the following paper we extend the study to the less well-understood vanadium(III) system.

Experimental Section

Preparation of Compounds. $Cs_2CrCl_5 \cdot 4H_2O$ was prepared by mixing without heating stoichiometric amounts of CsCl and green $CrCl_3 \cdot 6H_2O$ in 2 M HCl and letting the mixture evaporate slowly until crystals formed. The crystals are dark green, slightly dichroic, and not noticeably hygroscopic. When water is used as solvent, crystals are obtained which have spectra identical with those of the above compound.

Crystals were also prepared as follows: CsCl and Cr metal in a 2:1 molar ratio were dissolved separately in minimum amounts of water and 6 M HCl, respectively. The solutions were then mixed, filtered, and left to evaporate slowly. Another preparation was identical with this except that the mixture was refluxed 3 h before filtration. The spectra of the crystals formed in these latter two preparations are identical but differ in one polarization from the crystals made from $CrCl_3 \cdot 6H_2O$. This will be discussed below. Anal. Calcd for $Cs_2CrCl_5 \cdot 4H_2O$: Cr, 9.17; Cl, 31.26. Found: Cr, 9.28, 9.39; Cl, 30.98, 31.05, 31.00.

Deuterated crystals were obtained by dissolving stoichiometric amounts of CsCl and $CrCl_3 \cdot 6H_2O$ in a minimum amount of D_2O and evaporating to dryness over concentrated H_2SO_4 in a desiccator. The dry product was then redissolved in D_2O and evaporated in the same fashion until suitable crystals formed. The size of the water overtone bands in the near IR (ca. 1.7 μm) indicated that the degree of deuteration was about 95%.

Spectra. Polarized crystal spectra were measured at room temperature and ca. 10 K with use of a Cary 14 spectrophotometer and a Displex cryogenic refrigerator. A pair of calcite polarizers were used to polarize the radiation. Spectra were recorded from about 280 to 2200 nm with the electric vector of the light parallel to the extinction axes of the crystal. These latter are not colinear with any prominent crystal edge. The crystal was mounted over a hole in a thin copper disk (d = 2.5 cm) by means of Apiezon grease to which copper powder had been added to make it a better heat conductor.

Table II. Interatomic Distances (Å) and Angles (Deg) for $Cs_2CrCl_5 \cdot 4H_2O$

Cs–Cl(1)	3.484, 3.502, 3.571	Cs–Cl(3)	3.503
Cs–Cl(2)[a]	3.664, 3.709		
Cr–Cl(2)	2.302	Cr–O	1.925
Cl(1)–Cl(2)	3.814	Cl(2)–O	2.981, 3.021
Cl(1)–O[b]	3.006	Cl(3)–O[b]	3.062
O–O	2.715, 2.730, 3.411, 3.850		
<Cl–Cr–O	89.3, 90.8	<O–Cr–O	89.7, 90.4

[a] Cl(2) is coordinated to Cr. [b] Cl(1)–O and Cl(3)–O are H-bonded distances.

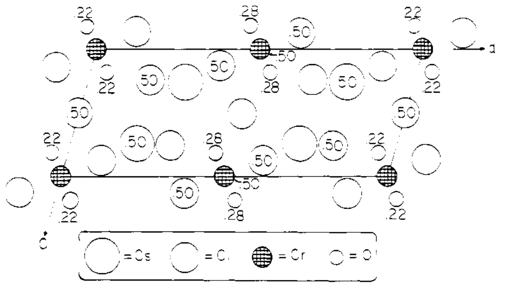

Figure 1. Unit cell of $Cs_2CrCl_5 \cdot 4H_2O$ looking down the b axis. The numbers on the atoms are their position above and below the ac plane in fractions of the unit cell b dimension.

X-ray Structure Determination. A crystal of dimensions, 0.08 × 0.48 × 0.06 mm was selected for data collection. Lattice constants were determined by a least-squares analysis of 55 centered reflections in the interval 34.2° < 2θ < 39.6°. Systematic absences observed in zero and upper level Weissenberg photographs were consistent with each of the space groups $C2$ (C_2^3), Cm (C_s^3), and $C2/m$ (C_{2h}^3). Integrated intensities for 1604 independent reflections with θ < 35° were measured on an Enraf-Nonius CAD-4 diffractometer using molybdenum Kα radiation (λ = 0.71073 Å). The structure was solved by trial and error methods taking into account the known stoichiometry and space group symmetry requirements.

Nonhydrogen atomic positions were refined in space group $C2/m$ by anisotropic full-matrix least squares. The final reliability index ($R = 100 \times \sum(|F_o| - |F_c|)/\sum|F_o|$) was 8.3% unweighted and 9.9% weighted for the 1140 observed reflections having $|F_o| > 2\sigma_F$. The R value was 12.6% for all reflections.

Results

X-ray Structure. $Cs_2CrCl_5 \cdot 4H_2O$ belongs to monoclinic space group $C2/m$ (C_{2h}^3), with the cell parameters, a = 17.604 (1) Å, b = 6.140 Å, c = 6.979 (1) Å, β = 106.040 (7)°, Z = 2, and d_{calcd} = 2.598 g cm^{-3}. The final atomic coordinates and thermal parameters are listed in Table I, and Table II contains the important interatomic distances and angles. Figure 1 shows a unit cell drawing looking down the b axis. The X-ray analysis shows that the compound is $Cs_2[CrCl_2(H_2O)_4]Cl_3$ and that the chromophore is trans.

Absorption Spectra. The polarized crystal spectra of $Cs_2CrCl_5 \cdot 4H_2O$ at 10 K from 13 × 10^3 to 37 × 10^3 cm^{-1} are shown in Figure 2; the crystal was one prepared from $CrCl_3$.

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[8] Ferguson, J.; Wood, T. E. *Inorg. Chem.* **1975**, *14*, 184, 190.

[9] McCarthy, P. J.; Lauffenburger, J. C.; Schreiner, M. M.; Rohrer, D. C. *Inorg. Chem.*, following paper in this issue.

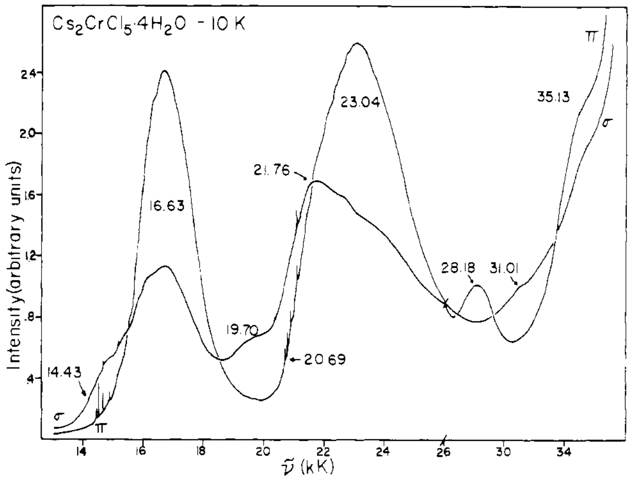

Figure 2. Polarized crystal spectra at 10 K of $Cs_2CrCl_5 \cdot 4H_2O$. Spectra are parallel (π) and perpendicular (σ) to the C_4 axis of the *trans*-$[CrCl_2(H_2O)_4]^+$ chromophore. Note scale change in $\tilde{\nu}$ at 26 × 10^3 cm^{-1}.

The labeling of the polarizations will be discussed below. It may be noted, however, that the complete polarization of the 19.70 × 10^3 and 28.18 × 10^3 cm^{-1} bands indicates no mixture of σ and π. Spectra recorded on the most prominent face of the crystals prepared from chromium metal yield two polarizations not perfectly separated; one is σ and the orthogonal polarization is mixed, largely π with some σ admixed. Therefore the 19.70 × 10^3 cm^{-1} band now appears in both spectra with different intensities. The different conditions of preparation cause different crystal faces to predominate.

The spectra show two broad bands in the visible region and in addition a third strong band at higher energy. The oscillator strengths of the broad bands at ca. 17 × 10^3 and 23 × 10^3 cm^{-1} are, respectively, 5 × 10^{-6} and 9 × 10^{-6} (σ) and 9 × 10^{-6} and 16 × 10^{-6} (π). All values are about ±20%. Two sets of weak, narrow bands are observed around 15 × 10^3 and 21 × 10^3 cm^{-1}. All these bands are readily identifiable features of the spectra of Cr(III) complexes. Other completely polarized bands at 19.70 × 10^3, 28.18 × 10^3, and 31.01 × 10^3 cm^{-1} are not normally seen in Cr(III) spectra. The maxima of the principal bands show upon cooling the usual shift to higher energy due to depopulation of the ground-state vibrational levels.

Discussion

Crystal Structure. Although crystalline $Cs_2CrCl_5 \cdot 4H_2O$ has no axis higher than C_2, the chromophore $CrCl_2O_4$ has almost perfect D_{4h} symmetry; all angles deviate less than 1° from 90°. The C_4 axis of the chromophore is perpendicular to the *b* axis of the unit cell and makes an angle of 3.2° with the long diagonal of the *ac* plane of the unit cell. When the hydrogens of water are added, D_{4h} symmetry of the chromophore is maintained if the water planes are either parallel or perpendicular to the Cl–Cr–Cl axis. The most stable configuration would be with the water planes parallel to Cl–Cr–Cl, since in this arrangement the waters are hydrogen bonded to eight chloride ions in the lattice. These latter occupy two different crystallographic sites, and the O–Cl distances in O–H---Cl are 3.006 and 3.062 Å. This indicates rather strong hydrogen bonding since the average distance found in such hydrogen bonds is about 3.08 Å.[10] Free rotation of the waters about the Cr–O axes will undoubtedly occur, but this will be minimized at low temperature. The Cr–Cl distance (2.302 Å) is nearly the same as that found in *trans*-$[CrCl_2(H_2O)_4]Cl \cdot 2H_2O$, namely, 2.289 Å^3. In the latter compound the Cr–O distances (2.004 and 2.006 Å) are, however, significantly longer than that in $Cs_2CrCl_5 \cdot 4H_2O$ (1.925 Å). The reason for this large difference is not known.

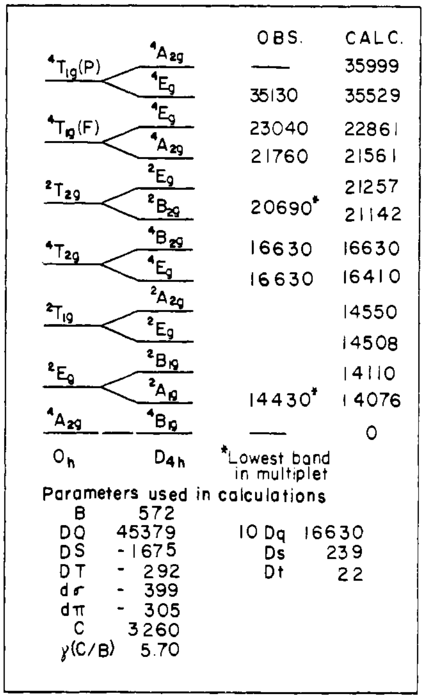

Figure 3. Energy diagram for $Cs_2CrCl_5 \cdot 4H_2O$ and the parameters used in calculating the transition energies. All data are in cm^{-1}.

Each Cs^+ ion is surrounded by eight chlorides (three coordinated and five free), and there are six different Cs–Cl distances between 3.48 and 3.71 Å. The resulting coordination polyhedron is very irregular but approximates a cube severely squashed in a direction approximately parallel to the Cl–Cr–Cl axis. The ionic radius of eight-coordinated Cs^+ is 1.88 Å and that of six-coordinated Cl^- is 1.67 Å.[11] The calculated Cs–Cl distance, 3.55 Å, is within the range of the distances observed in this crystal.

Interpretation of the Spectra. Spin-Allowed Bands. In the LF spectra of $Cs_2CrCl_5 \cdot 4H_2O$ at 10 K (Figure 2), the presence of oppositely polarized bands at 19.70 × 10^3 and 28.18 × 10^3 cm^{-1} suggests that the spectra taken along the extinction axes are actually spectra perpendicular (σ) and parallel (π) to the C_4 axis of the chromophore. These two bands have exact counterparts in the analogous vanadium complex in which the designation of the polarizations is certain. The polarization of the spectra containing the 19.70 × 10^3 and 28.18 × 10^3 cm^{-1} bands have accordingly been labeled σ and π, respectively, in the figure, and the designation is confirmed by the vibronic selection rules discussed below.[12]

The bands in both polarizations shrink greatly in size as the crystal is cooled. While the bands are not well separated, and the areas cannot be measured very accurately, the bands at 10 K are about 60 ± 10% the size at room temperature. This indicates that vibronic coupling is a principal means by which these forbidden transitions obtain their intensity.

The 15 normal vibrations of the *trans*-$CrCl_2O_4$ chromophore are as follows: ν(Cr–Cl) a_{1g}, a_{2u}; ν(Cr–O) a_{1g}, b_{1g}, e_u; δ(CrO_4 in-plane) b_{2g}, e_u; δ(CrO_4 out-of-plane) a_{2u}, b_{2u}, e_g; δ(ClCrCl) e_u. Coupling of the various u vibrations with the g electronic

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[10] Pimentel, G. C.; McClellan, A. L. "The Hydrogen Bond"; W. H. Freeman: San Francisco, 1960; p 292.

[11] Shannon, R. D. *Acta Crystallogr., Sect. A* **1976**, *A32*, 751.

[12] The exact face of the crystal upon which the spectra were recorded could not be determined; it is thought to be (101). Measurements on the (001) face, however, indicate that the spectrum labeled π in this paper is indeed exactly that.

states will give finite intensity to these forbidden transitions.

Figure 3 shows how the octahedral states split in D_{4h}, the symmetry of the chromophore; the ordering of the split components is explained below. The selection rules for D_{4h} indicate that all transitions are vibronically allowed in σ, but only $^4B_{1g} \rightarrow {}^4E_g$ in π. The other transitions are vibronically forbidden in π, since no a_{1u} or b_{1u} vibrations are available in the $CrCl_2O_4$ chromophore.

The principal bands in one polarization are clearly more complex than in the other; this polarization with multiple bands must then be σ. The bands which appear in both polarizations (16.63×10^3, 23.04×10^3, and 35.13×10^3 cm^{-1}) can accordingly be assigned to the transitions to the ^4E_g status. The transition to $^4A_{2g}[^4T_{1g}(F)]$ must then be at 21.76×10^3 cm^{-1} while that to $^4A_{2g}[^4T_{1g}(P)]$ is not observed. The 28.18×10^3 cm^{-1} band cannot be this latter $^4A_{2g}$ state, for it has the wrong polarization, and is too far removed from the 35.13×10^3 cm^{-1} band to be the other split component. Its nature is discussed below.

From the usual theory of quadrate complexes, if Dq(axial) < Dq(equatorial), as is the case here, then $^4B_{2g}$ must lie above the lowest ^4E_g.[13] This eliminates the weak shoulder ca. 14.7×10^3 cm^{-1} as $^4B_{2g}$. The weak band at 19.70×10^3 cm^{-1} can also be eliminated (see below). We may then assume that the broad band at 16.63×10^3 cm^{-1} in σ contains both split components which are only slightly separated. With the use of these assignments, transition energies were calculated by using the normalized spherical harmonic (NSH) Hamiltonian formalism,[14] and the differences between observed and calculated band energies for the spin-allowed bands were minimized. In this process four NSH parameters were used: DQ, DS, DT, and B. When this was accomplished a value of C was chosen which gave a reasonable fit for the spin-forbidden bands. These parameters were converted to the more usual ligand field tetragonal parameters and to the McClure dσ and dπ parameters[15] with the use of standard formulas.[14] These various calculated parameters are listed in Figure 3. It can be seen that $10Dq = 16.63 \times 10^3$ cm^{-1} and $B = 572$ cm^{-1}, both of which are in the proper range of values, and that d$\sigma = -399$ cm^{-1} and d$\pi = -305$ cm^{-1} (dσ is $\sigma_{\text{axial}} - \sigma_{\text{equatorial}}$ and similarly for dπ). The negative sign of these McClure parameters indicates that the σ- and π-bonding ability of water is greater than that of chloride ion. This is consistent with the data of Barton and Slade,[16] who found that both of the angular overlap bonding parameters, e_σ' and e_π' are larger for water than for chloride ion.

This interpretation is consistent with that given for the spectra of other quadrate complexes. For example, the polarized crystal spectra of *trans*-$[Cr(en)_2Cl_2]ClO_4$ (en = ethylenediamine), which also has weaker axial than equatorial ligands, show the same ordering of states.[17] A good fit between observed and calculated energies was had with $10Dq = 22.50 \times 10^3$ cm^{-1}, $B = 600$ cm^{-1}, $C/B = 5.0$, $Dt = -520$ cm^{-1}, and $Ds = -73$ cm^{-1}. These parameters gave values of d$\sigma = -1240$ and d$\pi = +1040$ cm^{-1}. Since ethylenediamine is a stronger σ donor than water, dσ is more negative than for our aquo complex. Likewise, the positive value of dπ indicates, as expected, that chloride ion is a stronger π bonder than ethylenediamine. Indeed, for the nitrogen donors in diamines, e_π' is often assumed to be equal to 0.[18]

The 19.70×10^3 cm^{-1} Band. This σ-polarized band shows two very weak structural features. It lies 3070 cm^{-1} above the 16.63×10^3 cm^{-1} band, which possesses the same weak structural features. This suggested that the higher energy band may be due to coupling of ν(OH) to some component(s) of the lower ligand field band. No band at 19.70×10^3 cm^{-1} is found in the deuterated complex. Instead, a band is found at 18.92×10^3 cm^{-1} in $Cs_2CrCl_5 \cdot 4D_2O$. The shift of the band on deuteration (3070/2290 = 1.34) correlates very well with frequency shifts in the IR spectrum of water. The OH (OD) stretching modes in water are 3652 (2666) cm^{-1} (symmetrical) and 3756 (2789) cm^{-1} (asymmetrical), and the ratios are equal to 1.370 (1.347).

Such coupling of OH stretches to electronic transitions in aquo complexes was first suggested by Piper and Koertge,[19] and was subsequently used by Harding et al.[20] and Shankel and Bates[21] to explain some weak features in the spectra of aquo complexes of Ni(II). The bands are also readily seen in the low-temperature spectra of $Ni(H_2O)_6^{2+}$ reported by Solomon and Ballhausen[22] and those of $Co(BrO_3)_2 \cdot 6H_2O$ discussed by Harding and Briat.[23] Ferguson and Wood[8] found similar, but more intense, features in the spectra of $CoCl_2 \cdot nH_2O$ (n = 6, 2). They found that these anomalous bands in $CoCl_2 \cdot 6H_2O$, which contains the *trans*-$[CoCl_2(H_2O)_4]$ chromophore, upon deuteration were shifted from their position in the nondeuterated complex, were strongly polarized along the x axis of the chromophore (x lies perpendicular to Cl–Co–Cl) and increased in intensity in a linear manner on cooling.

In $Cs_2CrCl_5 \cdot 4H_2O$ the 19.70×10^3 cm^{-1} band is also polarized perpendicular to the Cl–Cr–Cl axis, and it *seems* to get more intense on cooling. At room temperature, it cannot be seen in the spectra of the water complex and is barely visible in those of the deuterated complex. In both complexes, it is very clear at 10 K. But at room temperature the band may simply be obscured by the envelopes of the larger bands nearby. Therefore, its intensity behavior on cooling is not clear. In the analogous vanadium complex the band definitely increases in intensity on cooling and a possible reason for this will be discussed in the following paper.[9]

This band could be built on either component of the $^4T_{2g}$ (O_h) state. But since there is no similar band lying 3×10^3 cm^{-1} above the higher ligand field band ((21–23) $\times 10^3$ cm^{-1}), we might surmise that the 19.70×10^3 cm^{-1} band is built on the $^4B_{2g}$ (D_{4h}) component, the only excited state having this symmetry. The reason for this and for the complete σ polarization of the band is not known.

Spin-Forbidden Bands. In Cr^{3+} the zero-field splitting is less than 1 cm^{-1}.[24] Because of this, both spinor components of $^4B_{1g}$, namely, $E_{(1/2)g}$ and $E_{(3/2)g}$, will be significantly populated at all temperatures down to 10 K. Transitions are possible from both ground-state components to the five Kramers doublets in the 15×10^3 cm^{-1} region and to the three Kramers doublets in the 21×10^3 cm^{-1} region. Group theoretical analysis indicates that transitions to *all* these electronic states are allowed in D_{4h}' in *both* polarizations because of the availability in the chromophore of u vibrations of the proper symmetry. The sharp lines in the spectra starting at 14.43 $\times 10^3$ and 20.69×10^3 cm^{-1} in both polarizations can readily be assigned to transitions to states derived from the octahedral $^2E_g + {}^2T_{1g}$ and $^2T_{2g}$, respectively.

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In the first set of bands a sharp single spike appears at 14.43 × 10^3 cm^{-1} and may be the transition to ^2E_g (O_h) ($E_{(1/2)g}$ + $E_{(3/2)g}$ in D_{4h}'), which is calculated to lie below $^2T_{1g}$ (O_h). The position of the three spinor components of $^2T_{1g}$ (O_h) in D_{4h}' cannot be determined with certainty, since the spectrum between 14.4 × 10^3 and 17.7 × 10^3 cm^{-1} contains a large number of weak bands, most of which appear to be vibronic components associated with these spin-forbidden transitions. In the σ spectrum the last vibronic components are observed at 3050 and 3240 cm^{-1} above the 14.43 × 10^3 cm^{-1} band and represent the coupling of ν(OH) to the ^2E_g transition. In the deuterated compound the above two bands are missing and a new sharp spike appears 2420 cm^{-1} above the origin. This may be assigned to ν(OD) coupled to the ^2E_g transition. While in general the bands in this region are stronger in π than in σ, the highest energy component observed in π lies 2230 (H_2O) and 2270 (D_2O) cm^{-1} above the origin.

The complex of weak bands beginning at 20.69 × 10^3 cm^{-1} represents the transition to the three spinor components of $^2T_{2g}$ (O_h) plus vibronic components. The band contours are quite different in σ and π, again being more intense in π. In the π spectrum the highest vibronic component in the H_2O complex is about 3070 cm^{-1} above the lowest band; the spectrum of the D_2O complex is more poorly resolved, so the position of the highest component is not sure.

In the σ spectrum of the H_2O complex, a weak spike is found 2940 cm^{-1} above the lowest band, while in the D_2O complex a spike (missing in the H_2O complex) is seen at 2290 cm^{-1} above the lowest band. As in the case of the 14 × 10^3 cm^{-1} band these are probably ν(OH) and ν(OD) coupled to the lowest energy electronic transition.

It is not unusual to find such extensive vibronic structure on the ^2E_g + $^2T_{1g}$ bands. It is found, for example, in the spectra of the $Cr(H_2O)_6^{3+}$ ion[25] and of $Cr(en)_3^{3+}$.[26] In both cases vibronic bands are found at least 3 × 10^3 cm^{-1} above the origin bands. Such extensive structure on the $^2T_{2g}$ band seems to be less usually observed.

A complete analysis of these two band systems does not appear possible with the data presently available.

The 28.18 × 10^3 cm^{-1} Band. This band is completely π polarized. Calculations of energy states with use of reasonable LF parameters predict no spin-allowed band for $CrCl_2(H_2O)_4^+$ in this region. The band's intensity precludes its assignment as a spin-forbidden transition of this chromophore. It was noted that the two preparations starting with $CrCl_3$ and Cr metal gave crystals in which this band has different relative intensities. The suspicion that it was due to an iron impurity was confirmed by preparing crystals of the parent compound to which $FeCl_3$ was added. In these crystals the band at 28.18 × 10^3 cm^{-1} increased in relative intensity and so may be assigned to an electronic transition of the *trans*-$[FeCl_2(H_2O)_4]^+$ chromophore.

Since Fe^{3+} is a d^5 ion and when it is high spin as in this case, all its ligand field transitions are spin-forbidden and very weak, the band observed here must be due to an electron-transfer transition. The $CrCl_3$ used in the preparation of the complex contained ca. 0.008% Fe. This fact together with a comparison of the area of the impurity band with the areas of the bands of the chromium chromophore allows one to estimate that the molar extinction coefficient for the iron band is of the order of 10^4, and so it could be an allowed transition.

The energy of this band is not unreasonable for its assignment as an electron-transfer process in the $[FeCl_2(H_2O)_4]^+$ chromophore, since other iron–chlorine chromophores are expected to absorb in this region. For example, $FeCl_4^-$ shows an intense absorption beginning about 24.7 × 10^3 cm^{-1}.[27] Likewise, Jørgensen[28] has suggested that the first strong band in completely coordinated chloride complexes should follow the order: Re(IV) > Fe(III) > Os(IV). The first charge transfer in $ReCl_6^{2-}$ is centered at about 30.5 × 10^3 cm^{-1},[29] while the first parity-allowed charge transfer in $OsCl_6^{2-}$ is centered about 26.0 × 10^3 cm^{-1}.[30] So the transition in $FeCl_6^{3-}$ might be expected in the (26–30) × 10^3 cm^{-1} range.

Since this band is completely π polarized, the electric vector of the absorbed radiation oscillates in the Cl–Fe–Cl direction. If, as we suppose, the band is allowed and involves an electron transfer (most probably L → M), then it must be a Cl → Fe electron transfer.

The nature of the chlorine MO can be reasonably discerned from a group theoretical analysis. The ground state of the $FeCl_2(H_2O)_4^+$ ion is $^6A_{1g}$ (in D_{4h}). Transfer of an electron to the lowest energy iron orbital would create a ^5E_g metal state. Since the π dipole operator has symmetry A_{2u}, the ligand MO from which the electron comes must have symmetry E_u. The two symmetry-adapted linear combinations of the p_x and p_y orbitals on the two chlorines have symmetry E_u and E_g, and it is probable that the former of these is involved in the electron-transfer process.

In addition to the band at 28.18 × 10^3 cm^{-1} (π) there is another weaker band at 31.01 × 10^3 cm^{-1} (σ), whose intensity also varies in the same fashion as the 28.18 × 10^3 cm^{-1} band. It may also be assigned to the iron impurity. But little more than this can be said of it at present.

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Registry No. $Cs_2[CrCl_2(H_2O)_4]Cl_3$, 76773-10-9; $Cs_2CrCl_5 \cdot 4H_2O$, 76773-11-0; *trans*-$[FeCl_2(H_2O)_4]^+$, 53152-46-8; deuterium, 7782-39-0.

Supplementary Material Available: A listing of structure factor amplitudes (8 pages). Ordering information is given on any current masthead page.

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