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Crystal Structure, Low-Temperature Crystal Spectra, and IR Spectra of Tricesium Dichlorotetraaquovanadium(III) Chloride and Some Analogous Molecules

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X-ray diffraction has shown that $Cs_3VCl_6{\cdot}4H_2O$ belongs to orthorhombic space group *Immm* with unit cell parameters $a = 8.354$ Å, $b = 17.666$ Å, $c = 6.044$ Å, and $Z = 2$. The principal bond lengths are as follows: V–Cl, 2.377; V–O, 1.969; O–H···Cl, 3.038 Å. This last value indicates strong hydrogen bonding in the crystal. Since the VCl_2O_4 chromophore is trans and has nearly D_{4h} symmetry, the bands in the polarized crystal spectra have been assigned with the use of D_{4h} symmetry labels. Vibronic coupling is invoked as the principal intensity-gaining mechanism since the areas of the principal bands (16.43×10^3, 23.24×10^3, and 32.82×10^3 cm^{-1}) decrease markedly as the crystal is cooled. A band at 19.32×10^3 cm^{-1} (σ), however, increases in area as the temperature is lowered. Comparison of the spectra with those of the deuterated compound indicates that the band is due to coupling of ν(OH) of water with some component of the lowest spin-allowed band in the spectrum. Its intensity behavior can be rationalized in terms of the free rotation of the water molecules around the V–O axes and of the strong hydrogen bonding existing between each water and two chloride ions in the crystal. A π-polarized band at 29.33×10^3 cm^{-1} is due to an iron(III) impurity, and the band probably represents a low-energy charge transfer on the *trans*-$FeCl_2(H_2O)_4^+$ group. A group of very weak bands between 9.49×10^3 and 10.37×10^3 cm^{-1} are assigned as spin-forbidden transitions to states derived from ^1E_g and $^1T_{2g}$ in O_h.

Introduction

In the previous paper[2] we discussed the structure and spectra of the *trans*-$[CrCl_2(H_2O)_4]^+$ chromophore in $Cs_2CrCl_5{\cdot}4H_2O$. Here the study is extended to the analogous vanadium compound and some related molecules.

Several studies[3] of the aquo–halo complexes of vanadium(III) have been carried out, but only the structures of $VX_3{\cdot}6H_2O$ (X = Cl, Br) have been reported.[4] Both of these compounds contain the *trans*-$[VX_2(H_2O)_4]^+$ chromophore. To date, no low-temperature polarized crystal spectrum of any halo–aquo vanadium(III) complex has appeared. Such spectra of V(III) complexes are rather less abundant than those of many other metals of the first transition series. This may be due in part to the lability of the complexes with the consequent difficulty in preparation.

We have prepared the new compounds, $M_3VCl_6{\cdot}4H_2O$ (M = Cs, Rb) and $Cs_2VBr_5{\cdot}4H_2O$ and have determined the structure of $Cs_3VCl_6{\cdot}4H_2O$ by X-ray diffraction. The low-temperature polarized absorption spectra have been recorded and interpreted in terms of D_{4h} symmetry, the symmetry of the *trans*-$[VX_2(H_2O)_4]^+$ chromophores.

Experimental Section

Preparation of Compounds. $Cs_3VCl_6{\cdot}4H_2O$ was prepared by mixing CsCl and anhydrous VCl_3 in a ratio of 3:1 by weight (2.78:1.00 molar ratio) in a minimum of 2 M HCl without heating. The solution was filtered and allowed to evaporate slowly in contact with air. The compound separated as dark green rectangular plates. The crystals show extinctions along the major axes under crossed polarizers. Under polarized light they are strongly dichroic, appearing emerald green when the electric vector of the light is perpendicular to the long axis and faintly yellow-brown with the electric vector parallel to the long axis. The density of the crystal, determined by suspending it in a mixture of CH_2I_2 ($d = 3.33$ g cm^{-3}) and CH_3I ($d = 2.28$ g cm^{-3}), was found to be 2.74 g cm^{-3}. When exact stoichiometric quantities are used in preparing the compound, a solid white substance forms on the surface of the solution and the crystals grown are less suitable for optical spectroscopy. Anal. Calcd for $Cs_3VCl_6{\cdot}4H_2O$: Cs, 54.29; V, 6.94; Cl, 28.96. Found: Cs, 55.80; V, 7.08, 6.86; Cl, 29.42, 28.45.[5]

The partially deuterated compound was prepared in the same way as the nondeuterated compound. In this case a minimum of 2 M HCl, made by diluting 12 M HCl with D_2O, was used, and the solution was evaporated in a desiccator over concentrated H_2SO_4.

$Rb_3VCl_6{\cdot}4H_2O$ was prepared in the same way as the cesium analogue; the ratio of RbCl:VCl_3 was 2:1 by weight (2.58:1.00 molar ratio). The crystals are very similar to those of the cesium compound. Since they are more soluble in 2 M HCl, they form more slowly and so are of somewhat finer quality for spectroscopic study. On humid days they begin to decompose rapidly on contact with air. Anal. Calcd for $Rb_3VCl_6{\cdot}4H_2O$: Cl, 35.92. Found: Cl, 35.98.

$Cs_2VBr_5{\cdot}4H_2O$ was prepared by refluxing a weighed amount of vanadium metal in 48% HBr to which a small amount of Br_2 had been added to help oxidize the vanadium. When this was completed, a stoichiometric amount of CsBr was added. The resulting bright-green solution was transferred to a small beaker and allowed to evaporate in a desiccator containing a nitrogen atmosphere over solid KOH. Several weeks are required to get crystals. The process cannot be carried out in the atmosphere since the solution turns colorless overnight due to the atmospheric oxidation of V(III) in HBr. The crystals which separate are emerald green trapezoidal rods, which show dichroism similar to that observed for the analogous chloro complex. They are moderately stable in dry air. The density of the crystal was found to be 3.05 g cm^{-3}. It is not clear whether this tetrahydrate is really a different compound from the $Cs_2VBr_5{\cdot}5H_2O$ reported by Nicholls and Wilkinson[6] and Podmore and Smith;[3] the method of preparation of the two compounds is different. Anal. Calcd for $Cs_2VBr_5{\cdot}4H_2O$: Cs, 33.72; V, 6.46; Br, 50.68. Found: Cs, 33.60; V, 6.36, 6.54; Br, 50.43, 50.57.

Spectra. Polarized crystal spectra were measured at ambient temperature and 10 K (and in a few cases at various intermediate temperatures) with use of a Cary 14 spectrophotometer and a Displex cryogenic refrigerator equipped with a variable-temperature control unit. Calcite polarizers were used to polarize the incident radiation. Spectra were recorded from 200 to 2200 nm with the electric vector of the light parallel with the extinction axes of the crystal; these latter are colinear with the crystal and molecular axes (see below). The crystal was mounted over a hole in a thin circular copper disk (d = 2.5 cm) by means of Apiezon grease to which Cu powder had been added to make it a better heat conductor.

Infrared spectra were recorded from 30 to 4000 cm^{-1} on Beckman and Hitachi spectrophotometers at Marquette University (Milwaukee, WI).

X-ray Structural Determination. A crystal of dimensions, 0.56 × 0.43 × 0.16 mm was selected for data collection. Lattice constants

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

(2) McCarthy, P. J.; Lauffenburger, J. C.; Skonezny, P. M.; Rohrer, D. C. *Inorg. Chem.*, preceding paper in this issue.

(3) Podmore, L. P.; Smith, P. W. *Aust. J. Chem.* **1972**, *25*, 2521 and references cited therein.

(4) Donovan, W. F.; Smith, P. W. *J. Chem. Soc., Dalton Trans.* **1975**, 894 and references cited therein.

(5) Before the X-ray structure was done, it was thought that the compound contained three waters instead of four, and this erroneous formula was supplied with the crystal given to Dr. Richard Carlin (see ref 8).

(6) Nicholls, D.; Wilkinson, D. N. *J. Chem. Soc. A* **1969**, 1232.

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Table I. Fractional Coordinates and Anisotropic Thermal Parameters (×10⁴) for $Cs_3VCl_6 \cdot 4H_2O$ (Esd's in Parentheses)[a]

atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cs(1)	0	$^1/_2$	$^1/_2$	46 (2)	12	94 (4)	0	0	0
Cs(2)	$^1/_2$	0.1872 (1)	$^1/_2$	67 (2)	13	166 (4)	0	0	0
V	0	0	$^1/_2$	19 (4)	14 (1)	49 (9)	0	0	0
Cl(1)	0.2419 (5)	0.3429 (2)	$^1/_2$	44 (4)	15 (1)	172 (10)	−8 (3)	0	0
Cl(2)	0.2845 (6)	0	$^1/_2$	21 (4)	21 (2)	107 (11)	0	0	0
O	0	0.0794 (9)	0.2715 (27)	62 (15)	35 (5)	222 (38)	0	0	119 (22)

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

Table II. Interatomic Distances (Å) and Angles (Deg) in $Cs_3VCl_6 \cdot 4H_2O$

Cs(1)-Cl(1)	3.434	Cs(2)-Cl(1)	3.495, 3.675
Cs(1)-Cl(2)[a]	3.518	Cs(2)-Cl(2)[a]	3.766
V-Cl(2)[a]	2.377	V-O	1.969
Cl(1)-O	3.038	Cl(2)[a]-O	3.086
Cl(2)[a]-Cl(2)[a]	3.601		
O-O	3.937, 3.282, 2.763, 2.805		
Cl(2)[a]-V-O	90.0, 90.1	O-V-O	89.2, 90.9

[a] Cl(2) is coordinated to V.

were determined by a least-squares analysis of 15 centered reflections in the interval 30° < 2θ < 52°. Systematic absences observed in zero and upper level Weissenberg photographs were consistent with each of the space groups *Immm* (D_{2h}^{25}), *Imm*2 (C_{2v}^{20}), and *I*222 (D_2^8). Integrated intensities for 1109 independent reflections with $\theta < 45°$ were measured on an Enraf-Nonius CAD-4 diffractometer using Mo Kα radiation (λ = 0.71073 Å).

A Patterson map located the Cs, V, and one Cl atom. Subsequent *E* maps, phased with this original set of atoms, revealed the positions of the other nonhydrogen atoms. The nonhydrogen atomic positions were refined in space group *Immm* by anisotropic full-matrix least squares. The largest ratio of shift to estimated standard deviation in the final refinement cycle was 0.32, and unit weights were used. The final reliability index ($R = 100 \times \sum(|F_o| - |F_c|)/\sum|F_o|$) was 7.9% unweighted and 10.1% weighted for the 929 observed reflections having $|F_o| > 2\sigma_F$. The R value was 9.3% for all reflections.

Results

X-ray Structure. $Cs_3VCl_6 \cdot 4H_2O$ belongs to the orthorhombic space group *Immm* with cell parameters a = 8.354 (1) Å, b = 17.666 (3) Å, c = 6.044 (1) Å, Z = 2, and d_{calcd} = 2.734 g cm^{-3} (d_{obsd} = 2.74 g cm^{-3}). The final atomic coordinates and anisotropic thermal parameters are listed in Table I. Table II contains the interatomic distances and angles. In Figure 1 are two drawings of the unit cell with the views down the a and c axes.

Absorption Spectra. The polarized crystal spectra of $Cs_3VCl_6 \cdot 4H_2O$ at 10 K between 13 × 10³ and 37 × 10³ cm^{-1} are shown in Figure 2. The very weak bands (~10^{-2} as intense as the 23.24 × 10³ cm^{-1} band in π) in the (10–11) × 10³ cm^{-1} region are not shown but will be discussed below. The maxima of all bands show the usual shift to higher energy as the crystal is cooled. A third polarization perpendicular to the two shown here was also recorded; it is very like the weaker of those in Figure 2, differing only slightly in the relative intensities of the principal bands. Since the chromophore very nearly possesses D_{4h} symmetry, the labels of this point group have been used in assigning bands. The unique spectrum (light polarized perpendicular to the long axis of the crystal) can accordingly be assigned to the π spectrum (electric vector parallel to C_4); the other two are σ (electric vector perpendicular to C_4). The spectra of the rubidium analogue are very similar to those of the cesium compound.

The spectra of $Cs_2VBr_5 \cdot 4H_2O$ were recorded at room temperature and 77 K. They have features similar to those of the analogous chloro complex. The crystals are, however, much more irregularly shaped and appear to have lower symmetry than those of the chloro complex. The two polarizations are more similar to each other than in the chloro case and may both be σ–π mixtures. So it appears that the chromophores have a less favorable orientation relative to the crystal edges. In addition, no higher energy band could be observed due to a strong absorption beginning at ca. 27 × 10³ cm^{-1}.

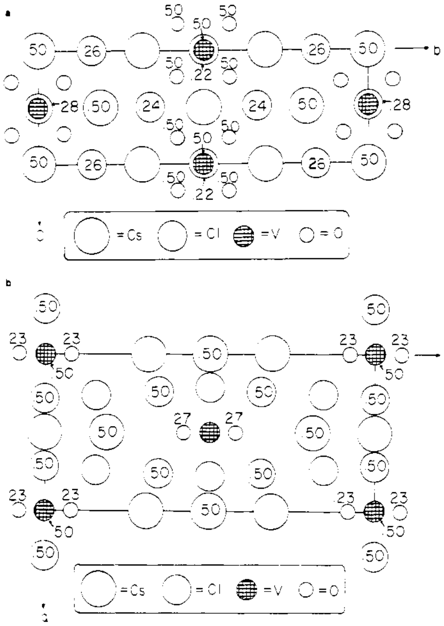

Figure 1. (a) Unit cell of $Cs_3VCl_6 \cdot 4H_2O$ looking down the crystal a axis. The numbers on the atoms are their positions above and below the bc plane in fractions of the unit cell a dimension. (b) Unit cell of $Cs_3VCl_6 \cdot 4H_2O$ looking down the crystal c axis. The numbers on the atoms are their positions above and below the ab plane in fractions of the unit cell c dimension.

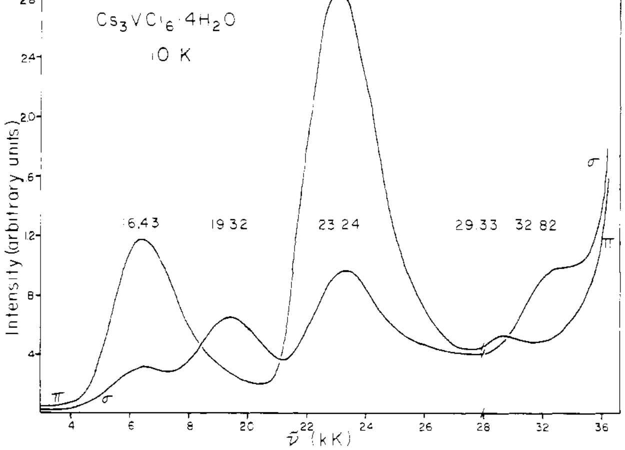

Figure 2. Polarized crystal spectra at 10 K of $Cs_3VCl_6 \cdot 4H_2O$. Spectra are || (π) and ⊥ (σ) to the C_4 axis of the *trans*-$[VCl_2(H_2O)_4]^+$ chromophore. Note scale change in $\tilde{\nu}$ at 28 × 10³ cm^{-1}.

Table III. Infrared Vibrational Frequencies (cm^{-1}) at Room Temperature

$Cs_3VCl_6 \cdot 4H_2O$	$Cs_3VCl_6 \cdot 4D_2O$	$Rb_3VCl_6 \cdot 4H_2O$	$Cs_2VBr_5 \cdot 4H_2O$[a]	assignt
~3200	~2380	c	~3200	$\nu(OH)\ a_{2u} + e_u$
1653	1447	1653	1603	$\delta(HOH)\ e_u$
1620	1426	1620	1588	
983	~985	~985	~990	?
740	b	745	757	$\rho w(H_2O)\ e_u$
610	b	615	560	$\rho r(H_2O)\ a_{2u}$
525 (sh)		526 (sh)		$\nu(V-OH_2)\ e_u$
	508		494	
511		516		
	395 (sh)[d]			?
356	360	355	311 (0.87)	$\nu(V-X)\ a_{2u}$
286	285	290	239 (0.84)	$\delta(VO_4$ in-plane$)\ e_u$
239	226	241	208 (0.87)	$\delta(VO_4$ out-of-plane$)\ a_{2u}$
204	204	205	195 (0.96)	$\delta(XVX)\ e_u$
140	c	140	140 (?)	lattice vibr (?)
120	c	120	113 (0.94)	lattice vibr (?)
64	c	84	80	lattice vibr
58	c	67	73	
45	c	52	64	
			55	
			46	
			35	

[a] Ratio of Cl/Br is in parentheses. [b] Exact position not clear from spectra. [c] Region not scanned. [d] 395/525 = 0.75 so this may be a water-related vibration.

Three bands are observed in the bromo complex at 15.87 × 10^3, 18.88 × 10^3, and 22.37 × 10^3 cm^{-1} (77 K). They have relative intensities similar to those in the analogous chloro complex. The observed bathochromic shift ((0.45–0.85) × 10^3 cm^{-1}) is expected for the substitution of bromine for chlorine in the chromophore since the former is lower on the spectrochemical series. In addition, a series of very weak bands beginning at 9.48 × 10^3 cm^{-1} is also observed in this compound. So it appears quite certain that the chromophore in the bromo complex is *trans*-$[VBr_2(H_2O)_4]^+$.

IR Spectra. The IR absorptions are listed in Table III together with a tentative assignment.

Discussion

Crystal Structure. Crystalline $Cs_3VCl_6 \cdot 4H_2O$ has no axis higher than C_2, but the chromophore *trans*-VCl_2O_4 possesses an axis which is very nearly C_4. The Cl–V–O angles are 90.0 and 90.1°, and the O–V–O angles are 89.2 and 90.9°. This C_4 axis is colinear with the *a* axis of the unit cell. The V–Cl and V–O distances, 2.377 and 1.969 Å, respectively, compare well with those found in *trans*-$[VCl_2(H_2O)_4]Cl \cdot 2H_2O$,[4] namely, 2.361 (V–Cl) and 1.961 and 2.023 Å (V–OH_2).

When the hydrogen atoms are added to the chromophore, D_{4h} symmetry is maintained if the plane of all four water molecules lie either parallel or perpendicular to the Cl–V–Cl axis. While at room temperature there will undoubtedly be some free rotation of the waters around the V–O axes, the principal orientation of the waters can be assumed to be parallel to Cl–V–Cl since in this arrangement hydrogen bonding is possible to eight nearby Cl^- ions. This will stabilize the parallel arrangement of the water planes. Such an arrangement will a fortiori predominate at 10 K because of reduced thermal motion.

If we assume that the plane of the water is parallel to the Cl–V–Cl axis, then the O–H···Cl angle is about 170°. It is the generally accepted view that this angle does not deviate from 180° by more than 10–15°.[7] This nearly linear arrangement coupled with the observed O···Cl distance of 3.038 Å indicates that rather strong hydrogen bonding should occur. Normally observed O–H···Cl distances average about 3.08 Å.[7] There appears to be some bending of the planes of the water molecules toward the *a* axis. This slight rhombic distortion may explain in part the small differences in intensity observed in the spectra of the two polarizations which should be identical in D_{4h}. Any rhombic distortion would be very small, however, since none was observed in the magnetic measurements of Carlin et al.[8]

The unusual stability of the crystals may be related to the hydrogen bonding which occurs and to strong interionic attractions in the crystal. In addition to the two vanadium complex ions there are six cesium ions in a unit cell. Two lie on one type of crystallographic site (Cs(1)) and four on another (Cs(2)). Cs(1) lies 3.518 Å from four bound chlorides, and these five atoms lie in the *ac* plane; the Cl–Cs–Cl angles are 61.6 and 118.4°. Cs(1) also lies 3.434 Å from four chloride ions, and these all lie in the *ab* plane, the Cl–Cs–Cl angles being 72.1 and 107.9°. For both sets the smaller angles are defined by two chlorides lying on an axis parallel to *a*. Thus the Cs^+ ion lies at the center of a solid figure which may be visualized crudely as a cube severely compressed along the *a* axis. Cs(2) is similarly surrounded by eight chlorides, two of them bound to V, and six free chloride ions. There are three different Cs–Cl distances: 3.766 Å to the bound chlorides, 3.674 Å to four Cl^- ions, and 3.494 Å to the other two Cl^- ions. The overall figure formed by the Cs(2) and eight chlorides is even more distorted than in the case of Cs(1) and its eight nearby chlorides. The ionic radius of 8-coordinated Cs^+ is 1.88 Å and that of 6-coordinated Cl^- is 1.67 Å.[9] The expected Cs–Cl distance is 3.55 Å, which is in the range of the distances found in this crystal.

Nature of the Chromophore. The chromophore in $VX_3 \cdot 6H_2O$ (X = Cl, Br) has been shown by X-ray crystallographic analysis to be *trans*-$[VX_2(H_2O)_4]^+$.[4] On the basis of IR and LF spectra, as well as other experimental data, it had earlier been suggested that the same chromophore is found in $VCl_3 \cdot 4H_2O$,[10] $KVCl_4 \cdot 6H_2O$,[10] $RbVCl_4 \cdot 6H_2O$,[3] $Cs_2VCl_5 \cdot 4H_2O$,[3] and $Cs_2VBr_5 \cdot 5H_2O$.[3,6] The similarity of the diffuse reflectance spectra of the above compounds with the crystal spectra of the compounds studied here indicates clearly that they all possess the *trans*-$[VX_2(H_2O)_4]^+$ group. The analogous group is also

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(7) Pimentel, G. C.; McClellan, A. L. "The Hydrogen Bond"; W. H. Freeman: San Francisco, 1960; pp 265, 292.

(8) Carlin, R. L.; O'Connor, C. J.; Bhatia, S. N. *Inorg. Chem.* **1976**, *15*, 985.

(9) Shannon, R. D. *Acta Crystallogr., Sect. A* **1976**, *A32*, 751.

(10) Horner, S. M.; Tyree, S. Y. *Inorg. Chem.* **1964**, *3*, 1173.

found in $CrCl_3{\cdot}6H_2O$,[11] $MCl_3{\cdot}6H_2O$ (M = Ti, Fe),[4] $CoCl_2{\cdot}6H_2O$,[12] $VBr_3{\cdot}6H_2O$,[4] and $Cs_2CrCl_5{\cdot}4H_2O$.[2] All crystallize in various monoclinic space groups.

Nature of the Electronic Ground State. According to the spectrochemical series, H_2O is a stronger ligand than Cl^-. The *trans*-$[VCl_2(H_2O)_4]^+$ chromophore is therefore equivalent to an octahedron distorted by elongation along C_4.[13] This makes $^3A_{2g}$ (from $^3T_{1g}(F)$) the expected ground state, which under spin-orbit coupling becomes $\bar{A}_{1g} + \bar{E}_g$. This is consistent with the magnetic anisotropy measurements carried out from 1.5 to 20 K on a single crystal of this compound by Carlin et al.[8] They found the ground state to be a singlet lying 8.05 ± 0.07 cm^{-1} below a doublet. At 10 K the relative population of the two levels is calculated on the basis of a Boltzmann distribution to be about 2 to 1. Transitions from both levels must then be considered when the electronic transitions are discussed.

The value of the ground-state splitting (D) (8.05 cm^{-1})[8] together with the value of the spin-orbit coupling constant (ζ) for the free V^{3+} ion (209 cm^{-1})[14] allows one to calculate an upper limit for the tetragonal splitting (δ) of the $^3T_{1g}(F)$ state. Since $D = \zeta^2/4\delta$,[14] δ is calculated to have a maximum value of 1357 cm^{-1}.

From the parameters listed by Jørgensen[15] for various complexes, one can estimate for $VCl_2(H_2O)_4^+$ a value of β, which is the ratio of B in the complex to the value of B for the free ion (861 cm^{-1}). β should be about 0.70 ± 0.05. A reasonable value of B for this complex is then ~600 ± 50. If the same reduction factor applies to the spin-orbit coupling constant, its value should be about 146 ± 10, and the $^3T_{1g}$ splitting (δ) should be ~670 ± 100 cm^{-1}.

Absorption Spectra: **Spin-Allowed Bands.** The optical spectra of the chloro complexes show above 13 × 10^3 cm^{-1} two bands (16.43 × 10^3 and 23.24 × 10^3 cm^{-1}) which appear in both polarizations. At 10 K these bands are respectively, 3.6 and 2.5 times as intense in π as in σ. At 10 K the areas of these two bands in π are only about 54% of their room-temperature values, and in σ they are about 66% of their room-temperature values. The spectra also show three bands which are completely polarized: 19.32 (σ) × 10^3, 29.33 (π) × 10^3, and 32.82 (σ) × 10^3 cm^{-1}. Of these, the first *increases* in area on cooling, being at 10 K about 34% larger than at room temperature. No exact measure of the area of the other two bands was possible. In the bromo complex, the two outer bands (15.87 × 10^3 and 22.37 × 10^3 cm^{-1}) decrease in size on cooling while the middle band (18.88 × 10^3 cm^{-1}) increases in size; no exact measurements of the areas have been carried out.

Since the two principal bands decrease in size when the crystal is cooled, a vibronic mechanism should be invoked to explain their intensity. As a first approximation we limit our attention to the VCl_2O_4 chromophore. The 15 normal vibrations are as follows: ν(V–Cl), a_{1g}, a_{2u}; ν(V–O), a_{1g}, b_{1g}, e_u; δ(VO_4 out-of-plane), a_{2u}, b_{2u}, e_g; δ(VO_4 in-plane), b_{2g}, e_u; δ(Cl–V–Cl), e_u. Coupling of the u vibrations to the d–d transitions can bring some intensity to these otherwise forbidden transitions. The application of vibronic selection rules indicates that all transitions are vibronically allowed in σ and π with the exception that $^3A_{2g} \rightarrow {}^3B_{1g}$ is allowed only in σ.

At this point, calculation of the band energies will be of substantial aid in the assignment. To calculate the transition energies we make use of the normalized spherical harmonic (NSH) Hamiltonian formalism.[16] The NSH parameters can be converted to the more usual ligand field parameters and to those of McClure[17] by standard formulas.[16]

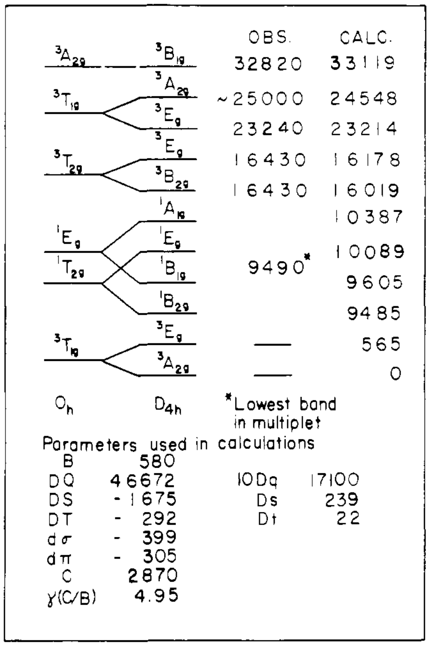

Figure 3. Energy diagram for $Cs_3VCl_6{\cdot}4H_2O$ and the parameters used in calculating the transition energies. All data in cm^{-1}.

Since the chromophore is analogous to $CrCl_2(H_2O)_4^+$, similar tetragonal parameters might be expected for the two chromophores. Using the values of DS and DT obtained for the Cr complex[2] together with B = 580 and DQ = 46 672 cm^{-1} (equivalent to $10Dq$ = 17 100 cm^{-1}), one obtains a reasonable fit for the spin-allowed bands. This value of B is close to that estimated above (600 cm^{-1}), and the value of $10Dq$ is reasonable. For example, $10Dq$ for the analogous Cr complex[2] was calculated to be 16 630 cm^{-1}, and the data listed by Jørgensen[15] indicate that $10Dq$ for V(III) is about 300–1400 cm^{-1} larger than that of Cr(III) in similar ligand fields. Figure 3 lists the parameter values as well as the calculated and observed energies. As in the case of the Cr complex, the splitting calculated for the band observed at 16.43 × 10^3 cm^{-1} is very small and is accordingly not seen in the spectra. The splitting of the second band (23.24 × 10^3 cm^{-1}), which is seen clearly in the Cr complex, is not obvious here. The band shape in π, however, indicates the presence of a weak shoulder around 25 × 10^3 cm^{-1}, near where $^3A_{2g}$ is calculated to appear. The $^3B_{1g}$ state is predicted to be at 33.12 × 10^3 cm^{-1} and is indeed found at 32.82 × 10^3 cm^{-1} and only in σ, as the vibronic selection rules predict. And finally, the tetragonal splitting calculated for the lower $^3T_{1g}$ state (565 cm^{-1}) is in reasonable agreement with that estimated above, namely, 670 ± 100 cm^{-1}.

While the 19.32 × 10^3 cm^{-1} band is not included in the above energy scheme, its possible assignment as one of the split components of $^3T_{2g}$ or $^3T_{1g}$ was not overlooked. A large number of computations were carried out under this assumption. All had to be rejected because of some major difficulty: either the fit between calculated and observed energies was very poor (root mean square deviation > 1 × 10^3 cm^{-1}) or it could be made acceptable only with unreasonable parameters (e.g., B = 218 cm^{-1}) or the calculations resulted in the assignment of the ground state as ^3E_g or the observed

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(11) Dance, I. G.; Freeman, H. C. *Inorg. Chem.* **1965**, *4*, 1555. Morosin, B. *Acta Crystallogr.* **1966**, *21*, 280.

(12) Mizuno, J. *J. Phys. Soc. Jpn.* **1960**, *15*, 1412. Joy, H. W.; Fogel, N. *J. Phys. Chem.* **1975**, *79*, 345.

(13) Webb, G. A. *Coord. Chem. Rev.* **1969**, *4*, 107.

(14) Carrington, A.; McLachlan, A. D. "Introduction to Magnetic Resonance"; Harper and Row: New York, 1967; p 160 ff.

(15) Jørgensen, C. K. "Absorption Spectra and Chemical Bonding in Complexes"; Addison-Wesley: Reading, MA, 1962; p 110 ff.

(16) Donini, J. C.; Hollebone, B. R.; Lever, A. B. P. *Prog. Inorg. Chem.* **1976**, *22*, 225.

(17) McClure, D. S. "Advances in the Chemistry of the Coordination Compounds"; Kirschner, S., Ed.; Macmillan: New York, 1961; p 498 ff.

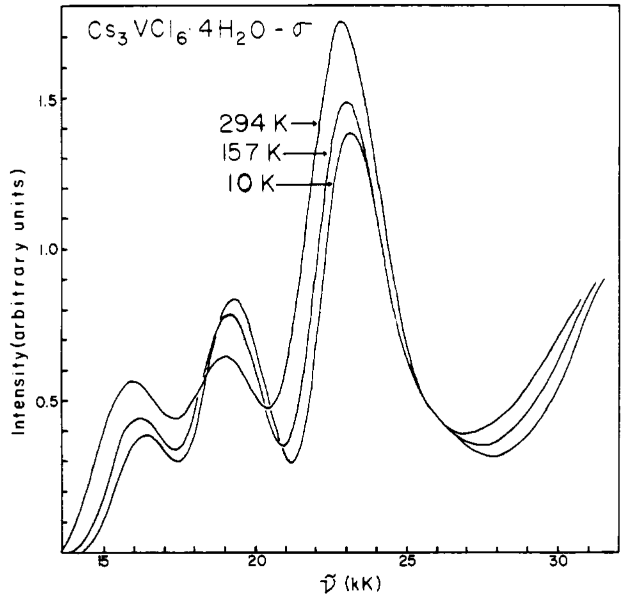

Figure 4. Polarized crystal spectra (σ) of $Cs_3VCl_6{\cdot}4H_2O$ at 10, 157, and 294 K.

polarization of the bands had to be completely ignored. This failure was in part responsible for the search which led to the assignment we present below.

Spin-Forbidden Bands. In the spectra of $Cs_3VCl_6{\cdot}4H_2O$, a series of very weak bands appears in both polarizations between 9.49×10^3 and 10.37×10^3 cm^{-1}; the bands are more numerous and intense in the π spectrum, about 15 being observed. The band positions are, in general, different in the two spectra. Transitions to four excited states are expected in this region: ${}^3A_{2g} \rightarrow {}^1A_{1g} + {}^1B_{1g}$ (from ${}^1E_g$ in O_h) and ${}^3A_{2g} \rightarrow {}^1E_g + {}^1B_{2g}$ (from ${}^1T_{2g}$ in O_h). Transitions to *all* excited spin–orbit states are vibronically allowed from *both* ground-state components in *both* polarizations except for the following: in π polarization, transitions from the $\bar{A}_{1g}$ ground-state component to $\bar{B}_{2g}$ and $\bar{A}_{2g}$ excited states are vibronically forbidden because of the absence of a_{1u} and b_{1u} vibrations in the VCl_2O_4 chromophore. With use of a reasonable value for C (2870 cm^{-1}), the spin-forbidden bands arising from the octahedral ${}^1T_{2g} + {}^1E_g$ states are calculated to appear in the range $(9.48\text{–}10.39) \times 10^3$ cm^{-1}. An unambiguous assignment of the bands does not, however, seem possible with the data at hand.

The 19.32×10^3 cm^{-1} Band. This band is σ polarized and increases significantly in area as the crystal is cooled (see Figure 4). At 10 K it lies 2890 cm^{-1} above the 16 430-cm^{-1} band. Upon deuteration the band shifts to lower energy, and lies 2370 cm^{-1} above the 16 430-cm^{-1} band; the shift ratio is 1.22. As in the case of the Cr complex,[2] the band gains its intensity by coupling of the LF band(s) at 16.43×10^3 cm^{-1} with ν(OH) of the coordinated waters. The eight OH stretches of the coordinated waters have symmetry a_{1g}, b_{1g}, e_g, a_{2u}, b_{2u}, and e_u. It is the a_{1g} vibration which is operative in the present case.

The fact that the band grows on cooling means that this coupling is more efficient at lower temperature. This in turn is probably related to the fact that the freedom of rotation of the waters around the V–O axes is lessened at low temperature. At 10 K the H bonding will be strongest and the waters will be more immobilized and locked into position. This somehow allows more efficient coupling of the O–H stretching vibration with the LF band(s).

In an attempt to quantify the relationship between the area of this band at 19.32×10^3 cm^{-1} and temperature, spectra were recorded at 11 temperatures between 10 and 312 K. About 100 points were read from each spectrum between 13.5×10^3 cm^{-1} (740 nm) and 27.8×10^3 cm^{-1} (360 nm), and each spectrum was resolved into three bigaussian bands. The best fit was found by an iterative computer program which also calculated the areas of the bigaussian bands. Ferguson and Wood[18] note that the intensities of the anomalous bands in the spectra of $CoCl_2{\cdot}6H_2O$ increase in a linear manner on cooling. In the present case, a plot of area vs. T (K) for the 19.32×10^3 cm^{-1} band gives a very poor linear relationship (linear correlation coefficient −0.965), while a plot of area vs. T^2 gives a considerably better one (linear correlation coefficient −0.998) (Figure 5). But it must be noted that the log (area) vs. T^2 relationship is nearly as good (linear correlation coefficient −0.994). It is probable that a slower scan rate in recording the spectra, together with the collection of more data points with use of computer-assisted data recording, would permit a more secure formulation of the area vs. T relationship. Any attempt to rationalize the relationship seems premature at the present time.

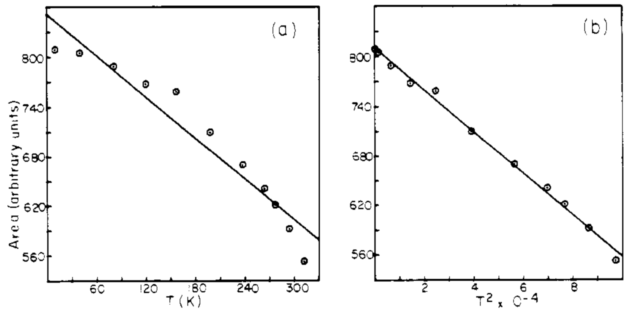

Figure 5. Area of the 19.32×10^3 cm^{-1} band of the σ spectrum of $Cs_3VCl_6{\cdot}4H_2O$ plotted (a) against T (K) and (b) against T^2 (K^2). The least-squares lines are shown.

The bands in the σ polarization of $Rb_3VCl_6{\cdot}4H_2O$ were similarly analyzed with similar results. The analogous band in the bromo complex surely grows as the crystal is cooled, but no band areas were calculated. We are not able to explain the polarization of the band at this time.

The 29.33×10^3 cm^{-1} Band. As in the case of the analogous Cr complex,[2] this π-polarized band is due to an iron impurity, since the band's intensity increases in the spectra of crystals to which $FeCl_3$ had been added. The π polarization is again explained if we assume, as in the case of the Cr complex, that the band is caused by a Cl → Fe electron-transfer process, possibly from an E_u MO formed from the p_x and p_y AO's of the chlorines. The band's position is about 1×10^3 cm^{-1} higher in energy than that in the Cr compound, even though it is probably due to the same process on the same chromophore, $FeCl_2(H_2O)_4{}^+$. This appears to be related to the fact that the M–Cl and M–O distances are 0.075 and 0.044 Å larger in the V complex than in the Cr. So in the latter case the nearer approach of the ligands would allow better M–L orbital overlap and thus lower the energy of the electron-transfer process. In addition to this, the electronegativity of Cr(III) is greater than that of V(III). This would also lower the energy of the electron-transfer process in the Cr compound. In the Cr complex a second band due to Fe was seen at 31.01×10^3 cm^{-1} in σ. This is not seen in the V complex since it would be expected $\sim 32 \times 10^3$ cm^{-1}, where in σ the transition to ${}^3B_{1g}$ is observed.

Spectra of $Rb_3VCl_6{\cdot}4H_2O$. The spectra of this compound are almost identical in appearance with those of the cesium analogue. The principal difference is that the maxima of all bands in the rubidium spectra are 300–800 cm^{-1} higher in energy than the corresponding bands in the cesium spectra. The principal maxima in the spectra of $Rb_3VCl_6{\cdot}4H_2O$ are

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

as follows (the energy differences between the Rb and Cs spectra are in parentheses, and all data are in cm^{-1}): 16 800 (370), 19 600 (280), 23 590 (350), 30 230 (900), and 33 610 (790). This indicates that the complexes are isomorphous, but that the different sizes of the 8-coordinated Rb^+ (1.75 Å) and Cs^+ (1.88 Å)[9] cause small differences in bond lengths in the chromophore together with a slightly stronger ligand field in the Rb compound.

IR Spectra. The bands which appear in the IR spectra (4000–35 cm^{-1}) of $Cs_3VCl_6{\cdot}4H_2O$ and related compounds are listed in Table III. Substitutions of Rb for Cs, Br for Cl, and D_2O for H_2O were made to make assignments more feasible. Since the chromophore has D_{4h} symmetry, the IR active bands belong to the a_{2u} and e_u representations. Of the bands below 1000 cm^{-1}, the former are ν(V–Cl), VO_4 (out-of-plane bend), and H_2O (rocking), and the latter are $\nu(V\text{–}OH_2)$, VO_4 (in-plane bend), ClVCl bend, and H_2O (wagging).

The bands ~3200, 1653, and 1620 cm^{-1} shift on deuteration and are clearly the H_2O stretching (a_{2u} and e_u) and bending (e_u) vibrations. The splitting of the latter band may be due to the fact that the H_2O molecules are strongly H bonded to the Cl^- in the lattice and the whole array should be considered in determining the selection rules. The bands at 740 and 610 cm^{-1} also shift markedly upon deuteration and are assigned to the H_2O wag and rock, respectively. This is the order suggested by Adams and Lock;[19] it is an inversion of the usual order proposed. In the deuterated compound these bands are much weakened, but the exact position of the D_2O bands is not very clear in the spectrum.

For hexahydrates of trivalent metals the IR active $\nu(M\text{–}OH_2)$ (ν_3) falls in the range 540–488 cm^{-1}.[20] This is the basis for the assignment of the strong band at 511 cm^{-1} in the chloro complex. The reason for the slight splitting in this band is not clear, but it may again be related to the strong H bonding of the $V(OH_2)_4$ group with eight Cl^- in the lattice. The band at 356 cm^{-1} shifts to 311 cm^{-1} on bromination. In $TiX_3{\cdot}6H_2O$ (X = Cl, Br), which most likely contain the *trans*-$[TiX_2(H_2O)_4]^+$ chromophores, bands at 336 (Cl) and 294 (Br) have been assigned to the titanium–halogen stretch.[21]

Without the introduction of factor-group analysis, one expects only three more IR-active low-frequency vibrations: $\delta(VO_4$ out-of-plane) a_{2u}, $\delta(VO_4$ in-plane) e_u, and δ(Cl–V–Cl) e_u. A *probable* assignment of these three is given in Table III. This is the same ordering given for $TiX_3{\cdot}6H_2O$.[21] The band at 239 cm^{-1} in the Cl^- complex is quite sensitive to deuteration and so may more probably represent out-of-plane motion of the VO_4 group. It should be remembered that in the crystal the waters tend to be held perpendicular to the VO_4 plane by H bonding. The X–V–X bend would be expected to lie below the VO_4 bends because of the greater masses of the halogens over oxygen. The above assignments agree with those given by Podmore and Smith[3] for $Cs_2VCl_5{\cdot}4H_2O$ and $Cs_2VBr_5{\cdot}5H_2O$.

All four vibrations in the range 195–360 cm^{-1} are lowered by substitution of Br for Cl, despite the assignment of two of them to $\delta(VO_4)$ vibrations. One of these latter has the same symmetry as the V–X stretch (a_{2u}) and the other the same as the X–V–X bend (e_u). Mixing of vibrations of the same symmetry could cause all four vibrations to be sensitive to halogen substitution.

This analysis would assign all vibrations below 150 cm^{-1} to vibrations involving O–H···Cl bonding and to lattice modes. Clearly some of these assignments are quite tentative, and full confirmation of them could be made only if normal coordinate analysis were carried out. Adams[22] has noted several things about the bands in this range: (1) they fall in the same region as metal–halogen bends and so can be difficult to separate from them; (2) they can, if they possess the correct symmetry, mix with and perturb nearby internal modes of the same symmetry; (3) they can be distinguished by their dependence on mass. Thus, when the counterion is changed (here Cs → Rb), the internal frequencies should remain the same while the lattice modes change. In the present case, the three lowest bands will be clearly lattice modes since they rise in energy when Rb^+ is substituted for Cs^+.

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Registry No. $Cs_3[VCl_2(H_2O)_4]Cl_4$, 76773-12-1; $Cs_3VCl_6{\cdot}4H_2O$, 70410-29-6; $Rb_3[VCl_2(H_2O)_4]Cl_4$, 76773-13-2; $Rb_3VCl_6{\cdot}4H_2O$, 76773-14-3; $Cs_2[VBr_2(H_2O)_4]Br_3$, 39710-53-7; $Cs_2VBr_5{\cdot}4H_2O$, 76773-15-4; *trans*-$FeCl_2(H_2O)_4^+$, 53152-46-8; deuterium, 7782-39-0.

Supplementary Material Available: A listing of structure factor amplitudes (6 pages). Ordering information is given on any current masthead page.

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(19) Adams, D. M.; Lock, P. J. *J. Chem. Soc. A* **1971**, 2801.

(20) Nakagawa, I.; Shimanouchi, T. *Spectrochim. Acta* **1964**, *20*, 429.

(21) Schläfer, H. L.; Fritz, H. P. *Spectrochim. Acta, Part A* **1967**, *23A*, 1409.

(22) Adams, D. M. "Metal-Ligand and Related Vibrations"; St. Martin's Press: New York, 1968; p 41.

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C,O-Chelates of the Trifluoroacetylacetonate Dianion with Platinum(II): Structure Assignment by means of ^1H, ^{13}C, ^{19}F, ^{31}P, and ^{195}Pt NMR Spectroscopy

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Bis(trifluoroacetylacetonato)platinum(II) reacted with triphenylphosphine, tris(*p*-chlorophenyl)phosphine, and triphenylarsine in diethyl ether or chloroform at room temperature to afford the [Pt(tfac(2–)-*C*,*O*)L_2] complexes. C,O-Chelation of the trifluoroacetylacetonate dianion in these complexes was confirmed by elemental analysis, molecular weight determination, IR and ^1H, ^{13}C, ^{19}F, ^{31}P, and ^{195}Pt NMR spectroscopy.

Acetylacetone and other β-dicarbonyl compounds are very versatile ligands[2] exhibiting various modes of bonding to metal ions as a neutral molecule[3] and a monoanion.[4] However compounds of the dianions are rather few, and only the sele-

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