tral data lead to the tentative picture of the concentrated, neutral $FeCl_3$ solution as being an array of $FeCl_4(H_2O)_2^-$ ions surrounded by a hydration sheath about a molecule thick and interstitial Fe^{+3} ions with very low coordination numbers. As for the exact coordination of the interstitial iron, 25% of the total, we do not feel that the data are sufficiently compelling to warrant saying anything more quantitative than that the coordination number is less than four. Again we have disregarded small amounts of other species such as $FeCl_4^-$ which while undoubtedly present would not contribute enough to the X-ray or spectral data to affect the results.[14]

Reasoning from the above we may suppose that one factor essential to the stability of the neutral solution structure is the hydration sheath which surrounds the $FeCl_4(H_2O)_2^-$ ions. We can regard the role of the H^+ ion as being a competitor for these H_2O molecules, in effect stripping them away from the octahedral ion to complete its own hydration sphere. The small size of H^+ makes it an extremely effective competitor in this process. We found also that in neutral concentrated $LiClO_4$ solutions of $FeCl_3$ the tetrahedral spectrum was again prominent, as would be expected in the presence of such a small ion. The formation of the tightly bound hydration layers around the small ions would lower the H_2O activity considerably and we could in fact look on this process as increasing the concentration of $FeCl_3$ and thus favoring the formation of polymer which, naturally, only would form in highly concentrated solution.

The octahedral to tetrahedral transformation is no doubt responsible for the maximum observed in the mass density of solutions of increasing HCl concentration (Fig. 4). It is, of course, extremely difficult to correlate mass densities with liquid structures because of their complexity, and we only cite the density data as giving qualitative support to the transformation.

It must be admitted that these models are speculative, and while a reasonably detailed structure of the acid solution can be postulated, that for the neutral solution is not as satisfactory. However, the important thing is that both the spectrophotometric and X-ray diffraction methods indicate unquestionably that the octahedral–tetrahedral transformation is caused by H^+ and Li^+ ions and that there is a fundamental structural difference between concentrated neutral and acid solutions of $FeCl_3$ and even between dilute and concentrated solutions of $FeCl_3$ in acid.

Acknowledgments.—We wish to acknowledge the technical assistance of N. A. Kuebler in the spectral work, and G. Wertheim for his measurements of the Mössbauer spectra. We also thank A. Ginsberg for some stimulating discussions.

(14) The presence of two different ion species in significant quantity in the neutral solution might be expected to yield two separate lines in the Mössbauer spectrum, if the solutions can be frozen. We found that all of the solutions, neutral and acid, freeze to clear, green glasses having the octahedral coordination spectrum. The Mössbauer spectra of the rigid glasses show a broad line which could be consistent either with two peaks indicating different isomer shifts for two different iron entities, or a very large quadrupole splitting. Unfortunately, little is known about the Mössbauer spectra of glasses and the results, while not inconsistent with our picture of the solutions, are not unambiguous.

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Chloro–Aquo Complexes of Vanadium(III)

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Preparations hitherto thought to be substances of stoichiometry $K_2VCl_5 \cdot nH_2O$ are shown by X-ray powder patterns to be fortuitous, equimolar mixtures of $KVCl_4 \cdot nH_2O$ and KCl. Two distinct substances are characterized, a green 6-hydrate and a red 1.5-hydrate, either capable of synthesis from the other by simple hydration or dehydration procedures. It appears to be impossible to dehydrate either completely to a simple chlorovanadate(III) complex. The green 6-hydrate has absorption bands at 16,050 and 22,990 cm.$^{-1}$, and the red 1.5-hydrate has bands at 19,300 and 12,580 cm.$^{-1}$. The compound $VCl_3 \cdot 4H_2O$ has been prepared by the dehydration of $VCl_3 \cdot 6H_2O$, both compounds exhibiting absorption spectra identical with that of $KVCl_4 \cdot 6H_2O$.

Introduction

Several red salts of $VCl_5 \cdot H_2O^{2-}$ were reported by Stahler,[1] and recently a green compound, $K_2VCl_5 \cdot 4H_2O$, was reported by Crayton and Thompson.[2] The latter workers also reported that the green compound dehydrates at 100–125° to pink anhydrous K_2VCl_5. When attempts to duplicate this dehydration failed, we undertook a study of these hydrates.

Experimental

Preparation of Compounds. (A) General Procedure for Preparing the Starting Solutions.—Anhydrous VCl_3 and KCl were dissolved in 150 ml. of 12 *M* HCl, such that the resulting solution was 0.5 *M* in VCl_3 and 1.0 *M* in KCl. Such solutions, being of the correct composition to produce $K_2VCl_5 \cdot nH_2O$, invariably produced $KVCl_4 \cdot nH_2O$ contaminated with KCl.

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(1) A. Stahler, *Ber.*, **37**, 4411 (1904).

(2) P. H. Crayton and W. A. Thompson, *J. Inorg. Nucl. Chem.*, **25**, 742 (1963).

TABLE I

Prepn. no.[a]	% V	% Cl	Cl/V	Oxidn. state of V	Calcd. for		
					Compd.	% V	% Cl
1B	13.55	48.01	5.09	3.07	$KVCl_4 \cdot 4H_2O + KCl$	13.46	46.84
1C	15.06	53.11	5.07	3.03	$KVCl_4 \cdot 1.5H_2O + KCl$	15.28	53.20
2A	12.38	43.67	5.07	3.01	$KVCl_4 \cdot 6H_2O + KCl$	12.29	42.77
2C	15.14	53.31	5.06	3.01	$KVCl_4 \cdot 1.5H_2O + KCl$	15.28	53.20
6A	12.39	45.09	5.22	3.03	$KVCl_4 \cdot 6H_2O + 1.2KCl$	11.86	42.95
6B	13.03	47.10	5.19		$KVCl_4 \cdot 4H_2O + 1.2KCl$	12.95	46.88
6C	14.51				$KVCl_4 \cdot 1.5H_2O + 1.2KCl$	14.62	
7A	15.66	41.51	3.81	3.04	$KVCl_4 \cdot 6H_2O + 0.2VCl_3 \cdot 6H_2O$	15.55	41.51
7C	19.62	52.88	3.83	3.12	$KVCl_4 \cdot 1.5H_2O + 0.2VCl_3 \cdot 4H_2O$	20.05	53.31

[a] A, green product isolated at −10°; B, red product obtained in HCl gas at room temperature; C, red product after heating in N_2 or HCl gas at 110°.

In the case of preparation no. 7, the ratio of VCl_3 to KCl was 1:1. It was usually necessary to warm the mixture for about 1 hr. to effect complete solution of the anhydrous VCl_3. The resulting solutions were clear green, and, in some cases, mixed with undissolved green crystals.

(B) **Isolation of Green Crystals.**—The green starting solutions were saturated with HCl gas for about 30 min. at −30 to −10°. Green crystals formed in large quantities and were removed immediately by filtration under nitrogen before the solution could return to room temperature. The crystals were dried by passing dry nitrogen through them, followed by being pumped on with a vacuum pump for 1–2 hr. at room temperature. Analyses indicated that the products were $KVCl_4 \cdot 6H_2O$, usually contaminated with varying amounts of KCl.

(C) **Isolation of Red Crystals.**—If the green crystals were allowed to stand in the HCl-saturated solution at room temperature for several hours, they turned a bright red. These latter crystals turned to a dull red upon filtration and drying in an atmosphere of HCl gas at room temperature. Analysis of the product corresponded to $[KVCl_4 \cdot 4H_2O + KCl]$. Treatment of the dry green crystals from part B with HCl gas at room temperature produced the same dull red product. Green crystals in which the ratio $KCl : KVCl_4 \cdot 4H_2O$ was >2 formed a lower hydrate by drying in HCl gas at room temperature.

Bright red crystals were obtained from either the dull red or the green crystals by heating to 110° in nitrogen or in HCl gas. Analyses indicated that these red crystals corrrespond to a 1.5-hydrate. It was found that an intimately-ground mixture of $VCl_3 \cdot 6H_2O$ and excess KCl, when heated to 110°, turned the same bright red color, and the product had a visible spectrum identical with those of the other red 1.5-hydrates. A solid-phase reaction is indicated here, since $VCl_3 \cdot 6H_2O$ alone does not undergo a similar reaction, although it will darken to red-brown upon much more prolonged heating.

(D) **Analytical Results.**—For ease of comparison, typical analyses of both green and red compounds are listed in Table I. The tabular form enables one to trace the product obtained on a single preparation through the successive treatments indicated.

(E) **Preparation of $VCl_3 \cdot 6H_2O$.**—A solution of 9.5 g. of anhydrous VCl_3 in 100 ml. of 12 *M* HCl was prepared by warming the mixture until a clear green solution was obtained. The solution was chilled to −10° and saturated with HCl gas. The green crystals of $VCl_3 \cdot 6H_2O$ were isolated in the same manner as described in part B. *Anal.* Calcd. for $VCl_3 \cdot 6H_2O$: V, 19.20; Cl, 40.09. Found: V, 19.22; Cl, 39.97; oxidation state of V, 3.05.

A portion of the product was allowed to stand under the solution at room temperature for several days. The product remained green, although a corresponding preparation of $[KVCl_4 \cdot 6H_2O + KCl]$ had changed to the red compound under the same conditions.

(F) **Preparation of $VCl_3 \cdot 4H_2O$.**—A sample of $VCl_3 \cdot 6H_2O$ was heated at 85–90° in a stream of HCl gas. The crystals lost water, but no visible color change occurred. After about 45 min., when no further H_2O was being evolved, the product was cooled in a stream of N_2. X-Ray powder pattern data show a pattern different from that of $VCl_3 \cdot 6H_2O$, although the visible spectrum remained unchanged. The infrared spectrum showed strong peaks at positions corresponding to H_2O stretching frequencies. *Anal.* Calcd. for $VCl_3 \cdot 4H_2O$: V, 22.21; Cl, 46.38. Found: V, 22.16; Cl, 45.88; Cl/V, 2.97.

Attempted Dehydration of $[KVCl_4 \cdot 1.5H_2O + KCl]$.—In order to verify that the 1.5-hydrate could not be dehydrated at elevated temperatures without decomposition, two preparations were subjected to heating in a stream of HCl gas. After 2 hr. at 140°, and some slight H_2O loss, the infrared spectrum of the first preparation still showed strong peaks at 3450 and 1600 cm.$^{-1}$, indicating the presence of H_2O,[3] and the visible spectrum was unchanged from that of the 1.5-hydrate. After 6 hr. at 190°, the color of the solid was a purplish red, and after 6–8 hr. more at 200°, the sample turned much darker with a very small amount of a red-brown liquid (presumably VCl_4) being evolved. The other preparation was heated at 170° for 3 hr., turning slightly purplish red with a small amount of H_2O being evolved, and then at 200° for 2 hr. with no further observable change. The infrared spectrum of the product showed strong H_2O bands, and a weak band attributable to the V=O stretching frequency[4] at 920 cm.$^{-1}$. A vanadium analysis indicated the product was still approximately a 1.5-hydrate. The visible spectrum was unchanged from that of the red 1.5-hydrate.

Reversibility of Color Change.—A green preparation (no. 2A) with analyses corresponding to $[KVCl_4 \cdot 6H_2O + KCl]$ was heated to 110°. The red product (no. 2C) gave analyses corresponding to $[KVCl_4 \cdot 1.5H_2O + KCl]$. After standing in a closed container over H_2O, the red product turned partially green. On being moistened with a few drops of H_2O, it turned brown, but upon evacuation for 2 hr. at room temperature, it turned back to a green powder. *Anal.* Calcd. for $K_2VCl_5 \cdot 6H_2O$: V, 12.29. Found: V, 12.09. In another experiment, wet nitrogen was passed over a red product. The product turned green, accompanied by the evolution of heat. In each case, the green preparation showed bands in the visible spectrum typical of the green 6-hydrate, while the red preparation displayed bands typical of the 1.5-hydrate.

Analyses.—Vanadium analyses were performed by reduction of a dilute H_2SO_4 solution of the sample in a Jones reductor. The reduced solution was caught in an excess of iron(III) sulfate solution. The resulting solution was titrated with a standard Ce(IV) solution.

The oxidation state of vanadium was determined by direct titration of the sample with a standard Ce(IV) solution.

Chloride was determined gravimetrically as silver chloride.

Spectra.—Samples of each product were ground in an agate mortar with KCl which had been fused and stored at 110°. The grinding was performed in a nitrogen-filled drybox. Portions of the bottled mixture were transferred quickly in air to a pellet die, the contents being layered so that the pressed pellet was coated on both sides by a layer of KCl. The pellet was pressed, and the

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(3) M. van Thiel, E. D. Becker, and G. C. Pimentel, *J. Chem. Phys.*, **27**, 487, 490 (1957).

(4) J. Selbin and S. P. McGlynn, Proceedings, Seventh International Conference on Coordination Chemistry, Stockholm, 1962.

TABLE II

Compound	Absorption maxima, Å.				
$[KVCl_4 \cdot 1.5H_2O + nKCl]$[a]		5,180		(7,660)	7,950
		[19,300 cm.$^{-1}$]		[13,050 cm.$^{-1}$]	[12,580 cm.$^{-1}$]
$[KVCl_4 \cdot 4H_2O + nKCl]$[a]	(4,350)	5,180	(6,200)	(7,650)	7,950
$[KVCl_4 \cdot 6H_2O + nKCl]$[a]	4,350		6,230		
	[22,990 cm.$^{-1}$]		[16,050 cm.$^{-1}$]		
$KVCl_4 \cdot 6H_2O$[b]	4,380		6,220		
$KVCl_4 \cdot 1.5H_2O$[b]	(4,400) w	5,180		(7,650)	8,000
$VCl_3 \cdot 6H_2O$	4,320		6,260		
$VCl_3 \cdot 4H_2O$	4,370		6,230		

[a] Positions of peaks are average values over about 30 determinations for all preparations containing excess KCl, originally thought to be $K_2VCl_5 \cdot nH_2O$. [b] Analyses showed these preparations to contain a small amount of $VCl_3 \cdot 6H_2O$.

visible spectrum was determined using a Cary Model 14 recording spectrophotometer and a pellet holder described previously.[5]

Infrared spectra were determined on similar, but more dilute, KCl pellets. All pellets examined showed very strong H_2O bands, although pure KCl pellets prepared under the same conditions showed only quite weak H_2O bands.

X-Ray Powder Patterns.—Powder patterns were determined on several representative samples of the preparations using a 114.59-mm. Norelco powder camera and Cu Kα radiation.

Results and Discussion

The experiments described indicate that $KVCl_4$ forms two distinct hydrates, one green and one red, and that the "compounds" $K_2VCl_5 \cdot nH_2O$ are probably in reality $[KVCl_4 \cdot nH_2O + KCl]$. X-Ray powder patterns were run on many of the preparations. In all products, both green and red, having a Cl/V ratio greater than 4:1, strong lines typical of the KCl powder pattern were observed, superimposed upon those of the compound being observed. In one product whose analysis corresponded to $KVCl_4 \cdot 6H_2O + 0.3KCl$, the KCl lines were rather weak. In preparation no. 7, with a Cl/V ratio of 3.8, no KCl lines were observed in either the red or green preparation.

Of all the compounds of the type $KVCl_4 \cdot nH_2O$ examined, only two different sets of powder patterns were obtained. One pattern was typical of the green 6-hydrate, and the second, different pattern was typical of the red 1.5-hydrates. Neither pattern corresponded to the sum of the patterns for KCl and $VCl_3 \cdot 6H_2O$ or $VCl_3 \cdot 4H_2O$. The latter fact indicates that $KVCl_4 \cdot 6H_2O$ is not a simple mixture of KCl and $VCl_3 \cdot 6H_2O$. However, the pattern for a "compound" of the formula $K_2VCl_5 \cdot 6H_2O$ corresponds to the sum of lines from the KCl pattern and of lines typical of $KVCl_4 \cdot 6H_2O$.

The positions of absorption maxima in the visible region are summarized in Table II. Contamination with KCl had no effect upon the spectra. Shoulders are given in parentheses.

Shoulders appear at about 5180 and 7800 Å. in the spectrum of green preparations which were subject to prolonged vacuum drying. On the other hand, red preparations, after exposure to moist air, develop shoulders at approximately 4350 and 6230 Å.

Consideration of X-ray and spectral data leads to the obvious conclusion that there are only two types of ligand fields surrounding the vanadium atom in $KVCl_4 \cdot nH_2O$. One is typified by the red 1.5-hydrate, the other by the green 6-hydrate. Thus products having analyses and colors in between the green and the red, such as the dull red 4-hydrate, are most likely mixtures of these two fundamental hydrates with distinctly different spectra and powder patterns.

All preparations, both green and red, dissolve readily in air-free H_2O to give brown solutions, with essentially all vanadium present as V(III). The absorption spectra of such solutions show bands at 4300 and 6350 Å., with molar extinction coefficients roughly estimated at 75 and 10, respectively. The similarity of these solution spectra to the pellet spectra of $KVCl_4 \cdot 6H_2O$, $VCl_3 \cdot 6H_2O$, and $VCl_3 \cdot 4H_2O$ indicates the probability of identical ligand fields.

It seems appropriate to speculate upon the nature of the ligand field in the compounds being considered. Studies by Furman and Garner[6] and others[7,8] show bands at 17,100 and 25,200 cm.$^{-1}$ for the $V(H_2O)_6^{3+}$ species. These bands are assigned, respectively, to the transitions $^3T_{1g}(F) \rightarrow {}^3T_{2g}(F)$ and $^3T_{1g}(F) \rightarrow {}^3T_{1g}(P)$ in the d^2 ion. The third spin-allowed band, $^3T_{1g}(F) \rightarrow {}^3A_{2g}(F)$, has been predicted by Ballhausen[9] to be at about 34,000 cm.$^{-1}$. Using Jørgensen's value[10] of 620 cm.$^{-1}$ for the Racah parameter B for $V(H_2O)_6^{3+}$, one calculates[11] a value of 18,400 cm.$^{-1}$ for $10Dq$.

In a study of the spectra of fused salts, Gruen and McBeth[12] report bands at 11,000 and 18,020 cm.$^{-1}$ in the spectrum of a melt containing VCl_6^{3-}. The bands correspond to the transitions $^3T_{1g}(F) \rightarrow {}^3T_{2g}(F)$ and $^3T_{1g}(F) \rightarrow {}^3T_{1g}(P)$, respectively. They report that these transitions agree well with a value of 12,000 cm.$^{-1}$ for $10Dq$. Using this value of $10Dq$ for VCl_6^{3-}, we calculate[11] a B value of 537 cm.$^{-1}$.

Presume an octahedral coordination for the vanadium(III) ion in the lattice of our preparations, and consider an "average ligand field" made up of a combination of Cl^- and H_2O ligands. The number of Cl^- and H_2O ligands in the hypothetical octahedral field can be estimated by comparing observed spectra with

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[5] S. M. Horner and S. Y. Tyree, *Inorg. Chem.*, **2**, 568 (1963).

[6] S. C. Furman and C. S. Garner, *J. Am. Chem. Soc.*, **72**, 1785 (1950).

[7] H. Hartmann and C. Furlani, *Z. physik. Chem.*, **9**, 162 (1956).

[8] L. E. Orgel, *J. Chem. Soc.*, 4756 (1952).

[9] C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill Book Co., Inc., London, 1962, p. 232.

[10] C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press, London, 1962, p. 110.

[11] Reference 10, p. 81.

[12] D. M. Gruen and R. L. McBeth, "The Coordination Chemistry of 3d Transition Metal Ions in Fused Salt Solutions," Plenary Lecture, Seventh International Conference on Coordination Chemistry, Stockholm, 1962, p. 34.

values interpolated between $V(H_2O)_6^{3+}$ and VCl_6^{3-}. For the interpolation we further assume that the values of B as well as those of $10Dq$ are linear between the two extremes and permit the prediction of the positions of absorption bands.

Using the determinant[11]

$$\begin{vmatrix} 15B - E & 0.4\,(10Dq) \\ 0.4\,(10Dq) & -0.6\,(10Dq) - E \end{vmatrix} = 0$$

to correct for interelectronic repulsions, and interpolating B and $10Dq$ values as indicated above, we calculate the positions for absorption bands shown in Table III.

TABLE III

Calculated Values

Ion	B, cm.$^{-1}$	$10Dq$, cm.$^{-1}$	$T_{1g}(F) \rightarrow T_{1g}(P)$, cm.$^{-1}$
$V(H_2O)_6^{3+}$	620	18,400	25,100
$V(H_2O)_4(Cl)_2^{+}$	592	16,300	22,800
$V(H_2O)_2(Cl)_4^{-}$	565	14,100	20,400
$V(H_2O)(Cl)_5^{2-}$	550	13,100	19,200
$V(Cl)_6^{3-}$	537	12,000	18,030

Observed Values

Preparation	$T_{1g}(F) \rightarrow T_{1g}(P)$, cm.$^{-1}$
$KVCl_4 \cdot 6H_2O$ (green)	22,990
$VCl_3 \cdot 6H_2O$ (green)	23,150
$VCl_3 \cdot 4H_2O$ (green)	22,880
$KVCl_4 \cdot 1.5H_2O$ (red)	19,300

The results strongly indicate that the compounds $KVCl_4 \cdot 6H_2O$, $VCl_3 \cdot 6H_2O$, and $VCl_3 \cdot 4H_2O$ contain vanadium in a site octahedrally surrounded by $4H_2O$ and $2Cl^-$ nearest neighbors, in the first approximation. Note that the largest number of H_2O groups which can surround vanadium in $VCl_3 \cdot 4H_2O$ without bridging is four, and its spectrum is identical with that of $VCl_3 \cdot 6H_2O$. (It should be pointed out that, considering the broad nature of the bands, the variations in peak positions of the three green compounds in Table III are within experimental error.) Also, X-ray studies have shown[13] that crystalline $CoCl_2 \cdot 6H_2O$ has four H_2O groups and two Cl^- groups in the first coordination sphere of the Co(II) ion. Also, $VCl_3 \cdot 6H_2O$ is a clear green, while V(III) alum, which must contain $V(H_2O)_6^{3+}$, is blue,[9] the two compounds therefore obviously having different spectra. Studies by Furman and Garner[6] on V(III) perchlorate solutions show the $T_{1g}(F) \rightarrow T_{1g}(P)$ band at 25,200 cm.$^{-1}$. Upon the addition of chloride to the solution, this band position shifts to 22,700 cm.$^{-1}$, again corresponding closely to that observed in our green preparations and brown solutions.

Using our hypothesis, the observed spectra of the red preparations would indicate a ligand field in the lattice of five Cl^- and one H_2O. Since $KVCl_4 \cdot 1.5H_2O$ only permits 5.5 ligands per vanadium, some bridging in the lattice must take place if six-coordination is maintained. Of course, H_2O bridging would permit a ligand field of four Cl^- groups and two H_2O groups. However, a compound with a large excess of KCl present gave analyses corresponding to a 1-hydrate ($KVCl_4 \cdot H_2O$ + 2KCl), and had a spectrum identical with those of all the other red compounds. Stahler's[1] description of his raspberry-red $K_2VCl_5 \cdot H_2O$ seems to match the appearance of the red preparations under consideration here. The evidence seems to favor Cl^- bridging in the lattice to give five Cl^- and one H_2O nearest neighbors.

Note should be taken of the double band at 13,050 and 12,580 cm.$^{-1}$ observed for the red compound. In a field of five Cl^- and one H_2O (or four Cl^- and two H_2O), a tetragonal splitting will be superimposed upon the octahedral field, splitting the $^3T_{1g}$ ground state into $^3A_2$ and ^3E states. It seems reasonable to assume that the double band results from transitions from these two low-lying states, apparently separated by about 500 cm.$^{-1}$, to the $^3T_{2g}$ state, which should also be split slightly.

Acknowledgment.—This work was supported by the Advanced Research Projects Agency.

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[13] J. Ferguson, *J. Chem. Phys.*, **32**, 533 (1960).