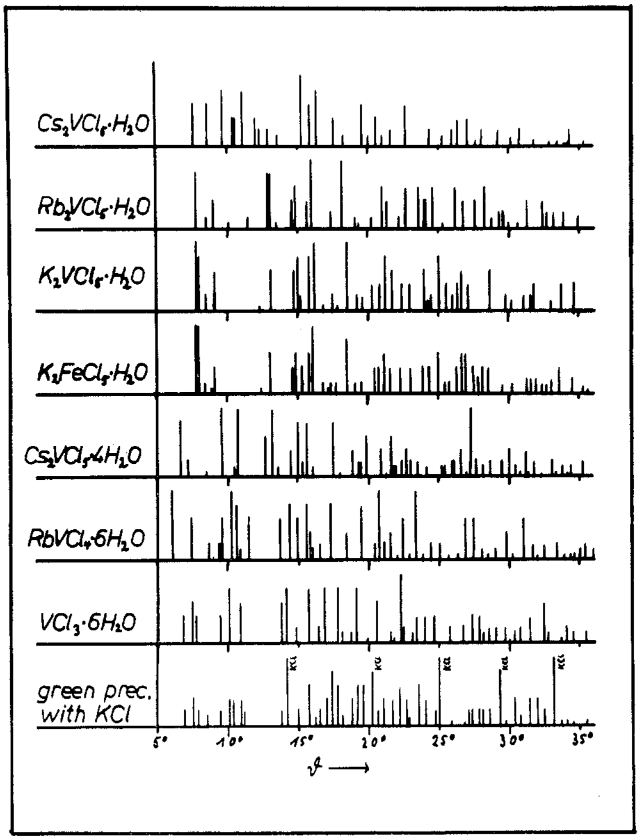

Figure 1.—X-Ray powder patterns (Cu Kα radiation).

TABLE I

DENSITIES AND MOLAR VOLUMES

Compound	Density, g cm^{-3}	Molar vol., cm^3
$Cs_2VCl_5\cdot H_3O$	2.985	172
$Rb_2VCl_5\cdot H_2O$	2.84	147
$K_2VCl_5\cdot H_2O$	2.31	140
$Cs_2VCl_5\cdot 4H_2O$	2.50	226
$RbVCl_4\cdot 6H_2O$	1.93	200

TABLE II

MAGNETIC MEASUREMENTS

	μ_{eff}, BM					μ_{eff} for V^{3+}
	275°K	206°K	100°K	θ, °K	Oxidn state	(room temp)
$VF_3\cdot 3H_2O$	2.88	2.83	2.79	−11	3.00	2.88
$VCl_3\cdot 6H_2O$	2.82	2.79	2.77	<|5|	2.99	2.81
$VBr_3\cdot 6H_2O$	2.77	2.73	2.80	<|5|	3.06	2.83
	286°K	196°K	82°K			
$Cs_2VCl_5\cdot 4H_2O$	2.85	2.82	2.81	<|5|	3.06	2.91
$RbVCl_4\cdot 6H_2O$	2.81	2.76	2.74	<|5|	3.08	2.89
$Cs_2VCl_5\cdot H_2O$	2.82	2.72	2.64	−20	3.05	2.87
$Rb_2VCl_5\cdot H_2O$	2.82	2.69	2.59	−30	3.08	2.90
$K_2VCl_5\cdot H_2O$	2.69	2.60	2.46	−20	3.11	2.80

Results

From hydrochloric acid solutions of vanadium(III) chloride and alkali chloride, MCl (M = Cs, Rb, K), two series of aquochloro complexes can be isolated. At elevated temperatures the red compounds $M_2VCl_5\cdot H_2O$ are found; at low temperatures green compounds containing more water are obtained.

$Cs_2VCl_5\cdot H_2O$ and $Rb_2VCl_5\cdot H_2O$ precipitate on introduction of HCl gas to the hot solutions. The potassium compound is obtained only after complete removal of water. To obtain the potassium compound free of KCl, the molar ratio VCl_3:KCl must exceed 1.5:2. (The theoretical ratio gives an incomplete reaction yielding a mixture of $K_2VCl_5\cdot H_2O$, KCl, and $VCl_3\cdot$aquo.) The complex chloride can be freed of the $VCl_3\cdot$aquo by washing with absolute ethanol. The composition of $K_2VCl_5\cdot H_2O$ is established in two ways: (1) Varying the molar ratio of VCl_3:KCl above the recommended 1.5:2 ratio always yields the same compound after the mixture has been washed with absolute ethanol. (2) X-Ray measurements show $K_2VCl_5\cdot H_2O$ to be isomorphous with the well-known $K_2FeCl_5\cdot H_2O$.

At 0° the green compounds $Cs_2VCl_5\cdot 4H_2O$ and $RbVCl_4\cdot 6H_2O$ were isolated. A green K compound could not be obtained in the pure state. However our results do not conflict with the existence of $KVCl_4\cdot 6H_2O$ described by Horner and Tyree;[4] a compound $K_2VCl_5\cdot 4H_2O$[3] must be excluded on the basis of analysis.

Thermal decomposition at 90° of $Cs_2VCl_5\cdot 4H_2O$ yields $Cs_2VCl_5\cdot H_2O$. At 60° $RbVCl_4\cdot 6H_2O$ is dehydrated to a mixture of $Rb_2VCl_5\cdot H_2O$ and hydrated vanadium(III) chloride; this latter compound can be removed by washing with absolute ethanol. It is assumed that the decomposition of the mixture $KVCl_4\cdot 6H_2O$ + KCl, described by Horner and Tyree,[4] is analogous to that of the rubidium compound. However, as described above, KCl and the $VCl_3\cdot$aquo react incompletely to yield more $K_2VCl_5\cdot H_2O$. Because Horner and Tyree did not remove the residue of hydrated vanadium(III) chloride, they described their red product as KCl + $KVCl_4\cdot 1.5H_2O$. Further decomposition was not achieved. As indicated above, pure $K_2VCl_5\cdot H_2O$ is dehydrated further to K_2VCl_5 at 250°.

In their spectral investigations of the red product, Horner and Tyree[4] found a field of five Cl^- and one H_2O around V^{3+}. This observation lends further support to the existence of $K_2VCl_5\cdot H_2O$.

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On the Reported Synthesis of Gallium Dodecaboride

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The existence of 11 isomorphous dodecaborides of rare earth and transition metals is known.[2] The reported unit cells are cubic, space group Fm3m, with

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[2] B. Post in "Boron, Metallo-Boron Compounds and Boranes," R. Adams, Ed., Interscience Publishers, Inc., New York, N. Y., 1964, p 326.

4 formula weights/unit cell; the lattice parameters are all close to 7.5 A. The only other dodecarborides known to be reported are three polymorphic forms of aluminum dodecarboride; α-AlB_{12} is tetragonal ($a = 10.16$ A and $c = 14.28$ A) and the β and γ forms are orthorhombic.[3]

In 1961, Chrétien and Lavéant reported the preparation of gallium dodecaboride (GaB_{12}).[4] They indexed the X-ray powder pattern on the basis of a tetragonal unit cell, with $a = 12.93$ A and $c = 4.84$ A. These results indicated the existence of a new type of metallic dodecaboride. An attempt was made to prepare single crystals of this compound for use in a three-dimensional crystal structure analysis.

Powder patterns of a number of samples prepared according to Chrétien and Lavéant's method of synthesis (heating pure gallium and boron in an evacuated quartz tube for about 24 hr at 1100–1300°) agreed with the pattern they reported. Small single crystals were found in three of the samples. A single-crystal X-ray diffraction investigation of one of these crystals showed it to be face-centered cubic with a lattice parameter of 5.43 A. It was subsequently identified as a single crystal of silicon. The powder pattern was reanalyzed after discarding those lines due to silicon, and the remaining lines were found to belong to a single-phase boron suboxide.[5] The apparent explanation for the formation of silicon is that the boron reduces the quartz.

Metallic gallium was undetected because the melting point of gallium (29°) is close to room temperature. Furthermore, the diffusivity of gallium into silicon dioxide at 1100–1300° is known to be large,[6] and a portion of the gallium can be assumed to have been adsorbed by the quartz crucible. However, X-ray diffraction rotation photographs taken of a few clusters of the polycrystalline material at $-20°$ did show the presence of gallium.

Further attempts were made to synthesize gallium dodecaboride in a quartz-free environment. This included (1) prolonged heating (15 hr) of stoichiometric amounts of gallium and boron in a boron nitride crucible in an electron-beam zone refiner, at temperatures up to 1800°, and (2) heating the elements together in a boron nitride crucible inside an evacuated quartz tube at about 1100° for 1 month. The only product formed was boron suboxide. It was probably caused by the reaction of boron with oxygen adsorbed in the boron nitride crucibles.

On the basis of the present investigation, it seems rather certain that gallium dodecaboride has not been synthesized. This confirms Seybolt's observation that gallium and boron do not react.[7]

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The Spectra of $[PtCl_4]^{2-}$ and $[PdCl_4]^{2-}$ in the LiCl–KCl Eutectic[1]

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In previous studies of the electronic absorption spectra of transition metal ions in fused-salt solvents, only octahedral or tetrahedral complexes (or distorted forms thereof) have been observed.[2] Since such studies can potentially yield information concerning the structure of fused salts, it seemed appropriate to investigate the effect of such a solvent on a square-planar complex. There has been considerable discussion of the assignments of the spectrum of the $[PtCl_4]^{2-}$ ion;[3–8] we have followed that of Chatt, Gamlen, and Orgel, which has been verified by Martin, Tucker, and Kassman. For the particular band of $[PdCl_4]^{2-}$ studied, we use the assignment of Day, *et al.*

Experimental Section

Spectra were recorded with a Unicam SP700 spectrophotometer; the furnace assembly and the method of preparation of solutions in the LiCl–KCl eutectic have been reported previously.[9]

Fused-quartz cells of 0.1-cm path length were used, sealed under vacuum. The LiCl and KCl used were Baker Analyzed reagent grade chemicals. The K_2PtCl_4 was Fisher "purified" material, while a sample of Cs_2PdCl_4 was prepared by precipitation with CsCl from a solution of Fisher $PdCl_2$ in 6 *N* HCl.

Results and Discussion

The spectra obtained are shown in Figures 1 and 2, with the band positions listed in Table I. The positions listed for the bands of K_2PtCl_4 in the LiCl–KCl eutectic have not been corrected for the effects of band overlap, as this is not necessary for the discussion which follows.

In discussing the changes observed in the spectra on changing the solvent and the temperature, three factors must be considered. These are (a) changes in the metal ion–ligand internuclear distance (and thus *Dq*) due to the thermal population of excited vibrational levels,[10] (b) a distortion toward tetrahedral symmetry, and (c) an orientation of solvent anions above and below the molecular plane to give a tetragonally distorted octahedral species.

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