CONTRIBUTION FROM THE INSTITUTE OF INORGANIC AND
ANALYTICAL CHEMISTRY,
JUSTUS LIEBIG UNIVERSITY, GIESSEN, GERMANY

# Chloroaquo Complexes of Vanadium(III)

BY HANS J. SEIFERT AND HANS W. LOH[1]

*Received March 8, 1966*

During our earlier investigations of vanadium(III) chloride complexes,[2a] we reexamined the red alkali compounds of $VCl_5 \cdot H_2O^{2-}$, first described by Stähler[2b] and reported in a method for the preparation of $K_2VCl_5 \cdot H_2O$ and for its dehydration to $K_2VCl_5$. In 1963 Crayton and Thompson[3] described a green compound $K_2VCl_5 \cdot 4H_2O$ which was dehydrated to pink $K_2VCl_5$ at 100–125°. These results were not duplicated by Horner and Tyree,[4] who found that from hydrochloric acid solutions only $KVCl_4 \cdot 6H_2O$ could be obtained. This compound was dehydrated to $KVCl_4 \cdot 1.5H_2O$. Because this latter work partially contradicts our results, a reinvestigation was undertaken. Additionally, the systems $CsCl–VCl_3–H_2O$ and $RbCl–VCl_3–H_2O$ have been studied and the magnetic susceptibilities and the densities of the compounds measured.

### Experimental Section

**Preparation of Compounds. (A) Isolation of Cs Compounds.**—When a solution containing 5 g of $VCl_3 \cdot 6H_2O$ and 3.5 g of CsCl in 40 ml of 6 *M* HCl was saturated with gaseous HCl at temperatures below 60°, a green precipitate was obtained. (In our experiments the temperature was maintained at 0°.) The green precipitate was separated by suction, washed with ether, and dried *in vacuo*. *Anal.* Calcd for $Cs_2VCl_5.4H_2O$: V, 9.00; Cl, 31.32. Found: V, 9.32; Cl, 31.38.

In the presence of a $CaCl_2$ desiccant and under reduced pressure the green precipitate was dehydrated to the red $Cs_2VCl_5 \cdot H_2O$ at a temperature of 80–90°. ($\Delta H_2O$: Calcd, 9.54%; Found, 9.80%.) Dehydration was also observed when the substance was kept for some time in ethanol. *Anal.* Calcd for $Cs_2VCl_5 \cdot H_2O$: V, 9.95; Cl, 34.62. Found: V, 10.02; Cl, 33.66.

**(B) Isolation of Rb Compounds.**—After introducing gaseous HCl into a solution of 5 g of $VCl_3 \cdot 6H_2O$ and 3 g of RbCl in 40 ml of 6 *M* HCl below 0°, green $RbVCl_4 \cdot 6H_2O$ precipitated. This precipitate was washed with ether and dried in a flow of nitrogen gas. *Anal.* Calcd for $RbVCl_4 \cdot 6H_2O$: V, 13.19; Cl, 36.71; $H_2O$, 27.90. Found: V, 13.23; Cl, 36.90; $H_2O$, 27.50.

At temperatures above 60° dehydration occurred in a vacuum desiccator to yield a red mixture of $Rb_2VCl_5 \cdot H_2O$ and hydrates of vanadium(III) chloride. Pure $Rb_2VCl_5 \cdot H_2O$ was obtained from the above solution by the method of Stähler.[2] The solution, in the presence of gaseous HCl, was heated on a water bath to reduce the volume of the liquid phase. *Anal.* Calcd for $Rb_2VCl_5 \cdot H_2O$: V, 12.21; Cl, 42.49. Found: V, 12.37; Cl, 42.90.

**(C) Isolation of K Compounds.**—Crayton and Thompson[3] reported the formation of a green compound $K_2VCl_5 \cdot 4H_2O$ by introducing gaseous HCl into a solution 12 *M* in HCl, 0.5 *M* in $VCl_3$, and 1.0 *M* in KCl; the temperature of the solution was maintained at −30°. The experiments of Horner and Tyree[4] yielded a green mixture of $KVCl_4 \cdot 6H_2O$ and KCl, by the above procedure. The crystals that formed were removed by filtration and dried first in a flow of nitrogen gas and then by being pumped on with a vacuum pump for 1–2 hr at room temperature. In our experiments KCl was precipitated from the above solution and also from solutions containing a $VCl_3$:KCl ratio of 1:1 by introduction of HCl gas. The green, crystalline precipitate, isolated at −30°, deliquesced in nitrogen to yield HCl. This strongly suggests that the mixture included hydrates of HCl which were stable below −15°.[5] After drying under reduced pressure the product was found to contain 7.2% V, 45.3% Cl, 13.5% $H_2O$, and 34.0% K, corresponding formally to a mixture of about 65% KCl and 35% $VCl_3 \cdot 6H_2O$. Since the X-ray pattern exhibited lines other than those for KCl and $VCl_3 \cdot 6H_2O$, at least one new compound must be present. By analogy to the results of Horner and Tyree[4] and to the rubidium system this new compound should be $KVCl_4 \cdot 6H_2O$.

Details for the preparation of the red $K_2VCl_5 \cdot H_2O$ have been given earlier.[2a] An excess of $VCl_3 \cdot 6H_2O$ was heated with KCl in a stream of HCl gas; the temperature was 100–120°. After treatment the excess of the vanadium(III) chloride hydrate was washed with absolute ethanol. *Anal.* Calcd for $K_2VCl_5 \cdot H_2O$: V, 15.70; Cl, 54.64. Found: V, 15.90; Cl, 54.62.

The red monohydrate can be dehydrated in a stream of HCl gas at 250–300° to the red-brown $K_2VCl_5$.

**X-Ray Powder Patterns and Densities.**—Powder patterns were determined by using a Berthold goniometer and Cu K$\alpha$ radiation (Figure 1). There is considerable evidence that the compounds $Rb_2VCl_5 \cdot H_2O$ and $K_2VCl_5 \cdot H_2O$ are isomorphous with the compound $K_2FeCl_5 \cdot H_2O$ described by Bellanca.[6] This compound crystallized in the orthorhombic $Cl_2[Rh(NH_3)_5Cl]$ type. $Cs_2VCl_5 \cdot H_2O$ should have a different structure. This is supported by the pycnometrical determinations in petroleum (Table I). By subtracting the increments *I* of the alkali ions $M^+$ ($2I_{K^+} = 32$ cm$^3$, $2I_{Rb^+} = 40$ cm$^3$, $2I_{Cs^+} = 52$ cm$^3$, as reported by Biltz[7]) from the molar volumes of the compounds $M_2VCl_5 \cdot H_2O$, the increment for the $VCl_5 \cdot H_2O^{2-}$ ion is obtained. The values for this ion are 108 and 107 cm$^3$ for the K and Rb compounds, respectively, and 120 cm$^3$ for the Cs compound. This indicates that the cesium compound is less tightly packed.

**Magnetic Measurements.**—Magnetic measurements were carried out with a Gouy balance. The magnetic field was standardized with $Hg(Co(CNS)_4)$,[8] and the temperatures were controlled by means of the dependence of the susceptibilities of nickel ammonia sulfate.[9] The $\chi_{mol}$ values were calculated as the average of measurements made on two samples. The values for $\mu_{eff}$ were obtained from the expression $\mu_{eff} = 2.84\,(\chi_{mol}^{cor}T)^{1/2}$. The values of $\theta$ were determined graphically from a plot of $1/\chi_{mol}$ *vs.* *T*. The error for $\mu_{eff}$ is ±0.03 BM and for $\theta$ is ±5°. The values of the oxidation state 3.00 for vanadium were extrapolated assuming that a change in the oxidation state of 0.01 would produce a change in $\mu_{eff}$ of 0.01 BM. Table II shows that at room temperature the values for $\mu_{eff}$ range from 2.80 to 2.90 BM which correspond to the spin-only value of 2.83 BM for two unpaired electrons. For those compounds with much water $\theta$ is zero within experimental error. For compounds with little water $\theta$ values range from −10 to −30°.

**Analyses.**—Vanadium was determined by titration with potassium permanganate. In determinations of the oxidation state of vanadium, the halides were removed by precipitation with a solution of silver sulfate (error ±0.03). The halides were determined by argentometric titration. Water was determined by the method commonly used for carbon–hydrogen analyses of organic compounds.

---

[1] Part of the dissertation of H. W. Loh, Giessen, Germany, 1966.

[2] (a) P. Ehrlich and H. J. Seifert, *Z. Anorg. Allgem. Chem.*, **301**, 282 (1959); (b) A. Stähler, *Ber.*, **37**, 4411 (1904).

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

[4] S. M. Horner and S. Y. Tyree, *Inorg. Chem.*, **3**, 1173 (1964).

[5] H. Remy, "Lehrbuch der Anorganischen Chemie," Akademische Verlags-Gesellschaft, Leipzig, 1960, p 929.

[6] A. Bellanca, *Ric. Sci. e Ricostruz.*, **17**, 1360 (1947); *Struct. Rept.*, **11**, 419 (1947).

[7] W. Biltz, "Raumchemie der festen Stoffe," Voss-Verlag, Leipzig, 1934, p 238.

[8] N. Figgis and J. Lewis in "Modern Coordination Chemistry," Interscience Publishers, New York, N. Y., 1960, p 415.

[9] P. Corsee, *J. Inorg. Nucl. Chem.*, **14**, 127 (1960).

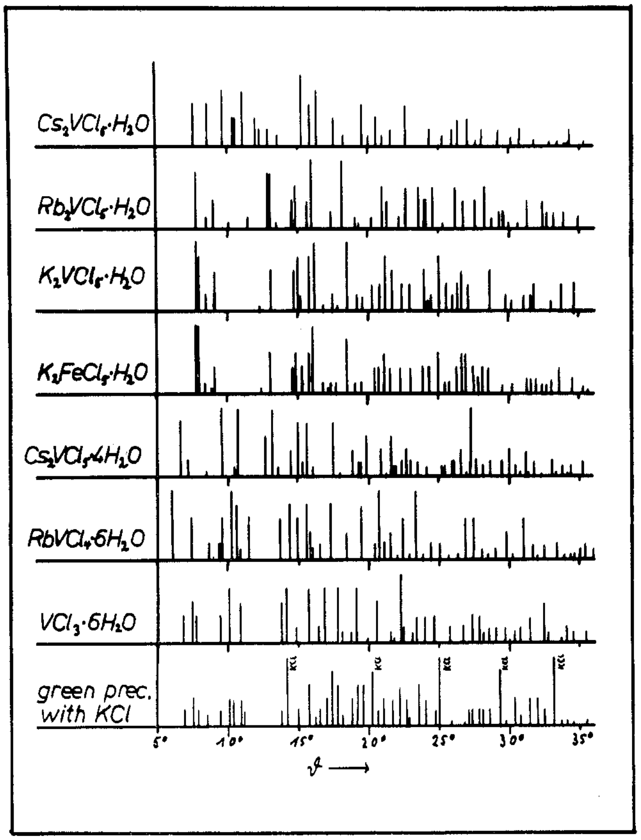

Figure 1.—X-Ray powder patterns (Cu Kα radiation).

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

| | $\mu_{eff}$, BM | | | | | $\mu_{eff}$ for $V^{3+}$ (room temp) |
|---|---|---|---|---|---|---|
| | 275°K | 206°K | 100°K | $\theta$, °K | Oxidn state | |
| $VF_3 \cdot 3H_2O$ | 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 $K_2VCl_5 \cdot H_2O$.

**Acknowledgment.**—This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

---

CONTRIBUTION FROM THE POLYTECHNIC INSTITUTE
OF BROOKLYN, BROOKLYN, NEW YORK 11201

## On the Reported Synthesis of Gallium Dodecaboride

BY REUBEN RUDMAN[1]

*Received April 6, 1966*

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

---

[1] Chemistry Department, Brookhaven National Laboratory, Upton, N. Y. 11973.

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