Crystal and Molecular Structures of Aquahalogenovanadium(III) Complexes. Part II.[1] *X*-Ray Crystal Structure of Dicaesium *trans*-Tetrakisaquadichlorovanadium(III) Trichloride, and the Isomorphous Bromo-compound

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Crystals of (I), Cs_2 *trans*-$[VCl_2(H_2O)_4]Cl_3$, are monoclinic, space group *C*2/*m*, with *a* = 17.745(8), *b* = 6.183(5), *c* = 7.019(5) Å, β = 106.4(5)°, and *Z* = 2. The structure was determined by Patterson and Fourier methods from visually estimated reflections and refined by full-matrix least squares to *R* 0.106. The hydrogen atoms were not located. Bond lengths within the complex cation are: V–Cl 2.361(2) and V–O 1.983(10) Å. For (II), the isostructural bromo-compound, *a* = 18.484(9), *b* = 6.423(5), *c* = 7.266(6) Å, β = 106.1(5)°, *Z* = 2. With *R* 0.17, bond lengths are: V–Br 2.497(1), V–O 2.060(7) Å.

IN Part I [1] of this series, the hydrated forms of vanadium(III) chloride and bromide were shown to contain the complex cation *trans*-$[VX_2(H_2O)_4]^+$ (X = Cl or Br). These compounds and salts of empirical formula $Cs_2VX_5\cdot4H_2O$ (X = Cl or Br) exhibit close similarities in chemical and physical properties.[2-4]

The structures of these caesium salts are now reported.

EXPERIMENTAL

Crystal Data.—(I) $Cs_2VCl_5\cdot4H_2O$. Monoclinic, *M* = 566.08, *a* = 17.745(8), *b* = 6.183(5), *c* = 7.019(5) Å, β = 106.4(5)°, *U* = 738.8 Å^3, *F*(000) = 268, D_c = 2.54 g cm^{-3}, *Z* = 2, D_m = 2.50 g cm^{-3}. μ(Cu-K_α) = 520 cm^{-1}. Space group *C*2/*m*. Cu-$K_{\bar{\alpha}}$ radiation, λ = 1.542 Å.

(II) $Cs_2VBr_5\cdot4H_2O$. Monoclinic, *M* = 788.36, *a* = 18.484(9), *b* = 6.423(5), *c* = 7.266(6) Å, β = 106.1(5)°, *U* = 828.8 Å^3, *F*(000) = 376, D_c = 3.16 g cm^{-3}, *Z* = 2, D_m = 3.20 g cm^{-3}. μ(Cu-K_α) = 549 cm^{-1}. Space group *C*2/*m*.

Cell dimensions for both compounds were refined by least-squares methods on data obtained from a Debye–Scherrer camera, with KCl as an internal calibrant.

The green crystalline solids were precipitated from aqueous solutions containing the related caesium and vanadium(III) halides on saturating with the appropriate hydrogen halide. The needle-shaped crystals were extremely sensitive to moisture and oxygen, which made mounting of single crystals difficult.

Structure Determination of the Chloride (I).—For (I) final data were collected from a crystal *ca*. 0.1 × 0.2 × 0.1 mm lodged in a thin-walled capillary sealed under nitrogen.

Trial zero-level equi-inclination Weissenberg *X*-ray photographs taken with Cu-K_α radiation showed the diffraction spots to be of reasonably regular shape. Noting this, and because of the difficulty referred to in mounting stable single crystals, non-integrated data were collected with minimum delay for several further levels *h*0—3*l* by the multiple-film Weissenberg technique. Attempts to photograph levels *h*4*l* and *h*5*l* showed only a few reflections of very poor resolution. However, the 243 observed reflections measured provided sufficient data for structure determination and refinement. The intensities of the reflections observed were estimated visually with a standard scale and were corrected for Lorentz and polarisation factors. No correction was made for absorption. The optimum thickness calculated for this compound is 0.04 mm. In neglecting absorption corrections, therefore, there is some decrease in the accuracy of measurements of intensity data. All calculations were performed as described previously.[1]

The Weissenberg photographs showed absent reflections *hkl*: $h + k = 2n + 1$. The space groups corresponding to these observations are *C*2/*m*, *Cm*, or *C*2.[5] In accordance with crystallographic practice, the centrosymmetric *C*2/*m* was chosen as the most likely space group and the subsequent structure determination confirmed this choice.

The main features of the structure were deduced by the conventional Patterson function method. Most of the significant interatomic vectors occur in the Harker plane (010) and in fact there are no peaks of any size outside this plane. With *Z* = 2 the vanadium atom could be fixed at the special position 2(*a*) 0,0,0 and most of the remaining scattering matter could be presumed to be in the (010) plane in real space. Analysis of the Patterson map provided positions for the caesium and chlorine atoms in this plane. This partial model was used to calculate structure factors corresponding to the observed reflections and the signs of the structure factors given to these observed values enabled Fourier and difference syntheses to be carried out. From these maps it was possible to locate the ligand oxygen positions. Data were then subjected to full-matrix least-squares refinement first on co-ordinates, and finally on co-ordinates plus isotropic temperature factors, *R* reducing to a final value of 0.104.

In these calculations the quantity minimised was: $D = \sum_h\sum_k\sum_l W_{(h,k,l)}(|F_o| - |kF_c|)^2$, where $W_{(h,k,l)}$ is a weighting factor usually given a unitary value. The standard deviations quoted were those calculated from the least-squares and bond-length computer program and for the errors in the positions of the heavy atoms due to uncertainties in the weighting scheme. They do not take into account errors in measurement of intensities and of unit-cell dimensions.

Interlayer scaling for the various levels of data was adjusted after each least-squares refinement cycle. Scattering curves used for the atoms involved were taken from ref. 5.

Under this refinement process the eight-fold oxygen position moved erratically and the temperature factor was

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[1] Part I, W. F. Donovan and P. W. Smith, *J.C.S. Dalton*, 1975, 894.

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[4] L. P. Podmore and P. W. Smith, *Austral. J. Chem.*, 1972, **25**, 2521.

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finally about twice the expected value, giving a V–O bond length of 1.85 Å. The water molecules are the only atoms outside the (010) plane and it is probable that because only four levels of data were collected along the *b* axis the least-squares refinement method concentrated all data errors in this direction on the *y* co-ordinate and temperature factor of the oxygen of the water molecule. The refinement process was, accordingly, repeated on the partial model without the water molecules. By locating the centre of the oxygen peak which occurred in the difference-Fourier at this stage, the atom was fixed at this position and further structure factors calculated. This gave a model with *R* 0.107, very nearly as low as that for the initial model. Variation of *x* and *z* co-ordinates of the oxygen reduced *R* marginally to 0.106. Fourier and difference-Fourier syntheses showed no anomalies for this model which was accepted as the final structure.

Structure Determination for the Bromide (II).—Inspection of *X*-ray powder data and single-crystal photographs suggested that (II) was isostructural with (I). Considerable difficulty was again experienced in mounting samples in capillaries for Weissenberg photography and the crystal finally used had dimensions 0.2 × 0.5 × 0.2 mm, although the calculated optimum thickness for this compound was *ca.* 0.04 mm. Data were collected about the monoclinic *b* axis for the five levels *h*0—4*l* giving a total of 511 observed reflections. Data were corrected for Lorentz and polarisation factors but not for absorption. Nevertheless, using a model derived by analogy with the chloride and proceeding by the methods described previously, calculations yielded a lowest residual factor of 0.17. At this value, Fourier and difference maps of the structure showed no anomalies, so refinement was terminated without correction for absorption.

RESULTS AND DISCUSSION

Atomic co-ordinates and isotropic thermal parameters for (I) and (II) are listed in Table 1. Final observed and calculated structure factors are to be found in Supplementary Publication No. SUP 21704 (6 pp., 1 microfiche).* Bond lengths and angles for both compounds are given in Table 2.

TABLE 1

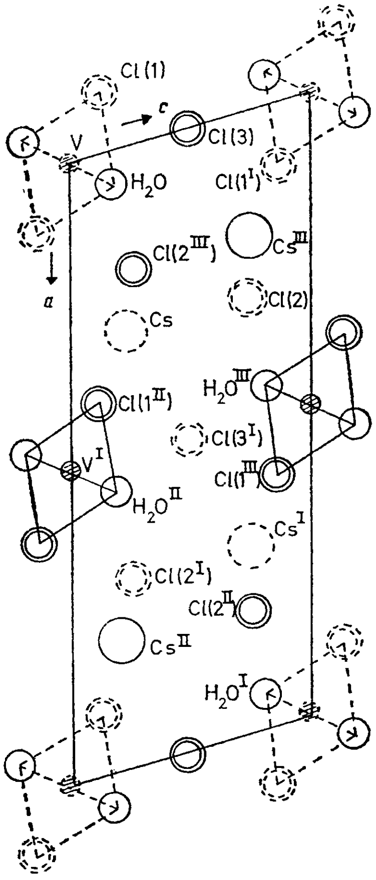
Fractional atomic co-ordinates and isotropic thermal parameters, with estimated standard deviations in parentheses

Atom	Position	*x*	*y*	*z*	$B/Å^2$
(*a*) (I), $Cs_2[VCl_2(H_2O)_4]Cl_3$					
V	2(*a*)	0	0	0	0.98(7)
Cs	4(*i*)	0.2980(1)	0	0.2442(1)	0.71(2)
Cl(1)	4(*i*)	0.1098(2)	0	−0.1275(5)	1.35(7)
Cl(2)	4(*i*)	0.3072(2)	0	0.7518(6)	1.76(7)
Cl(3)	2(*d*)	0	0.5	0.5	1.86(10)
$O(H_2O)$	8(*j*)	0.056(1)	0.209(2)	0.206(1)	2.99(20)
(*b*) (II), $Cs_2[VBr_2(H_2O)_4]Br_3$					
V	2(*a*)	0	0	0	1.01(5)
Cs	4(*i*)	0.2982(1)	0	0.2452(1)	1.19(2)
Br(1)	4(*i*)	0.1111(1)	0	−0.1325(2)	1.55(3)
Br(2)	4(*i*)	0.3070(1)	0	0.7473(2)	1.73(3)
Br(3)	2(*d*)	0	0.5	0.5	1.57(3)
$O(H_2O)$	8(*j*)	0.0506(4)	0.227(2)	0.193(1)	1.55(19)

TABLE 2

Molecular geometry with estimated standard deviations in parentheses; distances (Å), angles (°)

	(I)		(II)
(*a*) In the complex ion			
V–Cl(1)	2.361(2)	V–Br(1)	2.497(1)
V–O	1.983(10)	V–O	2.060(7)
Cl(1)–V–O	91.1(1)	Br(1)–V–O	90.3(2)
O–V–O	81.2(2)	O–V–O	90.2(2)
Cl(1) · · · O	3.054(8), 3.113(1)	Br(1) · · · O	3.229(6), 3.244(4)
(*b*) Other closest approach distances			
Cs · · · Cl(1)	3.612(1), 3.696(1)	Cs · · · Br(1)	3.775(1), 3.814(1)
Cs · · · Cl(2)	3.505(2), 3.520(3), 3.615(1)	Cs · · · Br(2)	3.607(2), 3.666(1), 3.763(2)
Cs · · · Cl(3)	3.528(1)	Cs · · · Br(3)	3.677(1)
Cl(1) · · · Cl(2)	3.828(2)	Br(1) · · · Br(2)	3.954(1)
Cl(2) · · · O	2.973(7)	Br(2) · · · O	3.091(5)
Cl(3) · · · O	3.102(5)	Br(3) · · · O	3.175(6)



The unit cell of (I), $Cs_2[VCl_2(H_2O)_4]Cl_3$, in projection down [010]. Open circles represent caesium atoms, double circles chlorine atoms, small open circles oxygen atoms, and hatched circles vanadium atoms. Atoms in the plane $y = 0$ are shown by dashed circles, atoms in the plane $y = \frac{1}{2}$ by full circles. Roman numeral superscripts I, II, III refer to the symmetry-related positions for a given atom

The structure of (I) is shown viewed along (010) in the Figure. The vanadium atoms are located at a two-fold special position. Each vanadium is at the centre of a complex ion $[VCl_2(H_2O)_4]^+$, the chlorine atoms of which are mutually *trans* with V–Cl 2.361 Å, and occupy four-fold positions such that Cl–V–Cl lies in the planes with $y = 0$ and $y = \frac{1}{2}$. The four ligand oxygens with V–O

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1975, Index issue. (Items less than 10 pp. are supplied as full-size copies.)

1.983(10) Å form a rectangular planar arrangement with the vanadium at the centre.

These bond lengths are in good agreement with those found[1] in *trans*-[$VCl_2(H_2O)_4$]Cl·$2H_2O$ where V–Cl is 2.361(2) and V–O 2.024(5) and 1.961(7) Å.

The complex ion is distorted from D_{4h} tetragonal symmetry, the bond angles being 91.1 for Cl–V–O and 81.2° for O–V–O. The O · · · O distances are 2.585 and 3.011 Å.

Of the remaining non-bonded chlorines, those labelled Cl(3) occupy two-fold equivalent positions and the Cl(2) atoms are in four-fold locations.

Each caesium ion is surrounded by eight chlorines as nearest neighbours; four of these are Cl(2) ions from two planes separated by $b/2$, one is a Cl(3) ion from the (010) plane, and the remaining three are Cl(1) ligands from three different octahedra. This arrangement is close to the CsCl body-centred cubic structure.

The nearest neighbours of the chloride ions Cl(2) form a distorted octahedron comprising four caesium ions, with Cs · · · Cl 3.505 and 3.520 Å and two ligand oxygens from different complex ions, with Cl · · · O 2.973 Å.

The other type of chloride ion Cl(3) is also surrounded by six nearest-neighbours occupying the corners of a slightly distorted octahedron. Two of these are caesium ions in the (010) plane, with Cs · · · Cl 3.528 Å; the others are ligand oxygens from four different complex ions, with Cl · · · O 3.102 Å. Each ligand chlorine, Cl(1), has three caesium ions, two at 3.696 and one at 3.612 Å as nearest neighbours.

The overall structure is thus one of close packing of Cs^+, [$VCl_2(H_2O)_4$]$^+$, and Cl^- ions in layers at $y = 0$ and $y = \frac{1}{2}$ perpendicular to the b axis.

Accordingly, the compound is formulated as Cs_2*trans*-[$VCl_2(H_2O)_4$]Cl_3.

The distances of closest approach of the chloride ions Cl(2) and Cl(3) to the ligand oxygens are <3.2 Å. Since the sum of ionic radii of Cl^- and O^{2-} is 3.21 Å, it is likely that there is some hydrogen-bonding between the chloride ions of one layer and co-ordinated water molecules of the octahedra centred in planes on either side of this layer.

Compound (II) is isostructural with (I) and the structure will not be further discussed, but comparisons can be drawn from the data listed in Tables 1 and 2.

The structures of these compounds can be compared with that of *trans*-[$FeCl_2(H_2O)_4$]Cl·$2H_2O$,[6] which also crystallises in space group $C2/m$ with $Z = 2$. In the vanadium compounds, two non-bonded halide ions occupy positions analogous to free water molecules in the iron compound. The caesium ions in the vanadium(III) structures are located in the (010) plane between the ligand halogens and the free halide ions. This gives rise to a much greater a axis and a slightly expanded c axis compared with those of the iron compound. The degree of apparent hydrogen-bonding in the vanadium compounds is much less than in the iron compound, because of the absence of water of crystallisation. The latter also precludes the existence of the hydrogen-bonded ' cages ' of water molecules reported for *trans*-[$CrCl_2(H_2O)_4$]Cl·$2H_2O$,[7,8] and postulated for [$FeCl_2(H_2O)_4$]Cl·$2H_2O$.

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