

## Crystal and Molecular Structures of Aquahalogenovanadium(III) Complexes. Part I. X-Ray Crystal Structure of *trans*-Tetrakis-aquadibromovanadium(III) Bromide Dihydrate and the Isomorphous Chloro-compound

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Crystals of (I), *trans*-[VBr<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>]Br·2H<sub>2</sub>O, are monoclinic, space group  $P2_1/c$ , with  $a = 6.408(4)$ ,  $b = 6.550(4)$ ,  $c = 12.300(7)$  Å,  $\beta = 96.15(5)^\circ$ , and  $Z = 2$ . The structure was determined by Patterson and Fourier methods from 372 visually estimated reflections, and refined by full-matrix least-squares to  $R$  0.11. V—Br 1s 2.539(1) and V—OH<sub>2</sub> 1.967(4) and 1.977(5) Å.

For (II), the isomorphous chloro-compound,  $a = 6.430(4)$ ,  $b = 6.439(4)$ ,  $c = 11.901(6)$  Å,  $\beta = 98.8(1)^\circ$ ,  $Z = 2$ ; 126 visually estimated reflections were refined to  $R$  0.12. Bond lengths are: V—Cl 2.361(2), V—OH<sub>2</sub> 2.024(5) and 1.961(7) Å.

An earlier study, by use of n.q.r. spectroscopy, had indicated that compounds with empirical formulae VBr<sub>3</sub>·6H<sub>2</sub>O and VCl<sub>3</sub>·6H<sub>2</sub>O contained covalently bonded halogen,<sup>1</sup> in accordance with other spectral evidence.<sup>2-4</sup> The present X-ray investigations were undertaken to obtain definitive evidence for the structures.

### EXPERIMENTAL

*Crystal Data.*—(I), VBr<sub>3</sub>·6H<sub>2</sub>O, Monoclinic,  $M = 398.77$ ,  $a = 6.408(4)$ ,  $b = 6.550(4)$ ,  $c = 12.300(7)$  Å,  $\beta = 96.15(5)^\circ$ ,  $D_c = 2.58$ ,  $Z = 2$ ,  $D_m = 2.48$  g cm<sup>-3</sup>. Space group  $P2_1/c$  from systematic absences. Cu- $K_\alpha$  radiation,  $\lambda = 1.542$  Å.

(II), VCl<sub>3</sub>·6H<sub>2</sub>O, Monoclinic,  $M = 265.40$ ,  $a = 6.430(4)$ ,  $b = 6.439(4)$ ,  $c = 11.901(6)$  Å,  $\beta = 98.8(1)^\circ$ ,  $D_c = 1.77$ ,  $Z = 2$ ,  $D_m = 1.65$  g cm<sup>-3</sup>. Space group  $P2_1/m$  or  $P2_1/c$ ; shown to be the latter. Cu- $K_\alpha$  radiation,  $\lambda = 1.542$  Å.

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

(I) Was precipitated from vanadium(III) bromide solution by evaporation and cooling as green crystals, unstable in air and moisture. For final data collection, a small needle-shaped crystal, *ca.* 0.2 × 0.1 × 0.1 mm, was coated with Nujol and sealed in a glass capillary. By use of Cu- $K_\alpha$  radiation, a total of 372 non-integrated equi-inclination Weissenberg reflections were recorded photographically on four-film packs for  $h0-3l$ . Intensities were estimated visually. Owing to the small size of the crystal used, no correction was made for either absorption or extinction. Data were corrected for Lorentz and polarisation factors.

The structure was solved by Patterson and Fourier techniques and refined by full-matrix least-squares to  $R$  0.11, the quantity minimised being  $\sum_h \sum_k \sum_l W_{(h,k,l)} (|F_o| - |kF_c|)^2$  where  $W_{(h,k,l)}$  is a weighting factor, usually given a unitary value. The standard deviations attached to the

resulting data account for those calculated from the least-squares and bond-length computer programs 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 the measurement of intensities and of unit-cell dimensions.

The sample of (II) was prepared from vanadium(III) chloride solution by evaporation and cooling as unstable green crystals. For what proved to be a twinned crystal, unit-cell dimensions and non-integrated intensity data for 427 reflections for the levels  $h0-4l$  were collected and treated as before.

Initial measurements had shown the compound to be monoclinic with absent reflections for  $0k0$  with  $k = 2n + 1$ , suggesting space group  $P2_1/m$ . This cell had dimensions of  $a = 6.420$ ,  $b = 6.439$ , and  $c = 23.802$  Å and  $\beta = 98.8^\circ$ . Early attempts to solve the structure on this basis were unsuccessful. Comparison of the powder data with those for VBr<sub>3</sub>·6H<sub>2</sub>O showed close similarity. Examination of the Weissenberg photographs suggested that the reflections from VCl<sub>3</sub>·6H<sub>2</sub>O were in reality from a twinned crystal. By use of the unit cell of (I) as a guide it was found possible to resolve the twins of (II). The crystals can be considered as being twinned across the (010) plane such that their reciprocal lattices share  $b^*$  and  $c^*$  axes, with  $a^*$  axes of each twin oriented at  $2\beta^* 162.4^\circ$  to one another. This has the effect of removing an extinction due to the glide-plane of the single crystal in space group  $P2_1/c$  and giving the twinned lattice the higher symmetry of  $P2_1/m$ . It was fortunate that the superposition of one crystal lattice on the other is not exact and it became possible to distinguish the reciprocal lattices from one another. This made it a relatively simple matter to draw appropriate nets for the lattices of each twin, and to record the reflections unique to one of the crystals.

<sup>3</sup> D. Nicholls and D. N. Wilkinson, *J. Chem. Soc. (A)*, 1969, 1232.

<sup>1</sup> L. P. Podmore, P. W. Smith, and R. Stoessiger, *Chem. Comm.*, 1970, 221.

<sup>4</sup> L. P. Podmore and P. W. Smith, *Austral. J. Chem.*, 1972, **25**, 2521.

<sup>2</sup> S. M. Horner and S. Y. Tyree, *Inorg. Chem.*, 1964, **3**, 1173.

The reflections corresponding solely to the strong twin were extracted and corrected for Lorentz and polarisation factors. No correction was made for absorption. Of 427 reflections from the twinned material, 126 unique single-crystal reflections were used for the structure refinement process.

A model derived from the structure of the bromine compound was adapted to account for the smaller V-Cl as compared to V-Br bond lengths, and this model was used for refinement of the  $VCl_3 \cdot 6H_2O$  structure. The refinement was carried out by the full-matrix least-squares method to  $R$  0.12.

The shifts in parameters in the final cycle were within the standard deviations. Final Fourier and difference maps showed no anomalies. The 126 reflections used provided over five reflections per variable in the final refinement cycles, and gave satisfactory values to the variable parameters and also for the bond lengths and angles which were calculated from them.

TABLE 1

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

(a) (I)  $[VBr_2(H_2O)_4]Br \cdot 2H_2O$

Atom	$x$	$y$	$z$	$B/\text{\AA}^2$
V	0.0	0.0	0.0	1.05(2)
Br(1)	0.50	0.0	0.50	1.71(1)
Br(2)	0.2812(1)	-0.0239(1)	0.1615(1)	1.97(1)
$OH_2(1)$	0.8048(5)	-0.0199(8)	0.3016(3)	1.91(6)
$OH_2(2)$	0.1905(6)	0.1286(8)	-0.0948(3)	2.16(9)
$OH_2(3)$	-0.0729(6)	0.2674(8)	0.0602(3)	2.58(9)

(b) (II)  $[VCl_2(H_2O)_4]Cl \cdot 2H_2O$

V	0.0	0.0	0.0	1.93(6)
Cl(1)	0.50	0.0	0.50	1.43(8)
Cl(2)	0.2707(3)	-0.0293(6)	0.1577(2)	3.59(6)
$OH_2(1)$	0.7813(8)	0.0097(17)	0.2979(5)	3.44(15)
$OH_2(2)$	0.1931(9)	0.1490(14)	-0.0927(5)	3.04(15)
$OH_2(3)$	-0.0761(10)	0.2621(12)	0.0656(5)	3.49(16)

Calculations were made on an Elliott 503 computer using a suite of X-ray crystallographic programs by Finney.<sup>5</sup> 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. 6.

Atomic co-ordinates and isotropic thermal parameters for both compounds are given in Table 1. Final observed and calculated structure factors are listed in Supplementary Publication No. SUP 21266 (8 pp., 1 microfiche).\*

## RESULTS AND DISCUSSION

Figure 1 shows the unit cell for (I) in projection down  $[010]$ . The vanadium atoms are located at  $(0,0,0)$  and  $(0,1/2,1/2)$  and are surrounded by six ligands, two bromines mutually *trans* and four water molecules, forming a distorted octahedral environment around the central metal. The distortion from tetragonal  $D_{4h}$  symmetry is small, the Br-V-OH<sub>2</sub> and H<sub>2</sub>O-V-OH<sub>2</sub> bond angles differing by  $\leq 3^\circ$  from  $90^\circ$  and the two H<sub>2</sub>O...OH<sub>2</sub> distances being nearly equal. Dimensions in the complex ion are shown in Table 2.

The overall arrangement of the  $[VBr_2(H_2O)_4]^+$  ions and the remaining bromide ions and water molecules is

\* See Notice to Authors No. 7, in *J.C.S. Dalton*, 1974, Index issue.

shown in Figure 1. The centres of the two complex ions in the unit cell are located in equivalent positions

TABLE 2

Molecular geometry with estimated standard deviations in parentheses. Distances ( $\text{\AA}$ ) and angles ( $^\circ$ )

(a) In the complex ion			
	(I)		(II)
V-Br(2)	2.539(1)	V-Cl(2)	2.361(2)
V-OH(2)	1.967(4)	V-OH <sub>2</sub> (2)	2.024(5)
V-OH <sub>2</sub> (3)	1.977(5)	V-OH <sub>2</sub> (3)	1.961(7)
Br(2)···OH <sub>2</sub> (2)	3.298(2)	Cl(2)···OH <sub>2</sub> (2)	3.053(6)
Br(2)···OH <sub>2</sub> (3)	3.313(3)	Cl(2)···OH <sub>2</sub> (3)	2.999(7)
H <sub>2</sub> O(2)···OH <sub>2</sub> (3)	2.747(7), 2.828(5)	H <sub>2</sub> O(2)···OH <sub>2</sub> (3)	2.784(11), 2.852(7)
Br(2)-V-OH <sub>2</sub> (2)	93.2(1)	Cl(2)-V-OH <sub>2</sub> (2)	92.1(1)
Br(2)-V-OH <sub>2</sub> (3)	93.15(1)	Cl(2)-V-OH <sub>2</sub> (3)	92.6(2)
H <sub>2</sub> O(2)-V-OH <sub>2</sub> (3)	88.3(2)	H <sub>2</sub> O(2)-V-OH <sub>2</sub> (3)	88.6(2)
(b) Other closest-approach distances			
Br(1)···OH <sub>2</sub> (1)	3.287(2)	Cl(1)···OH <sub>2</sub> (1)	3.229(4)
Br(1)···OH <sub>2</sub> (2)	3.273(4)	Cl(1)···OH <sub>2</sub> (2)	3.097(7)
Br(1)···OH <sub>2</sub> (3)	3.150(4)	Cl(1)···OH <sub>2</sub> (3)	3.111(6)
Br(2)···OH <sub>2</sub> (1)	3.334(5)	Cl(2)···OH <sub>2</sub> (1)	3.015(10)
H <sub>2</sub> O(1)···OH <sub>2</sub> (2)	2.644(3)	H <sub>2</sub> O(1)···OH <sub>2</sub> (2)	2.684(6)
H <sub>2</sub> O(1)···OH <sub>2</sub> (3)	2.675(5)	H <sub>2</sub> O(1)···OH <sub>2</sub> (3)	2.809(9)

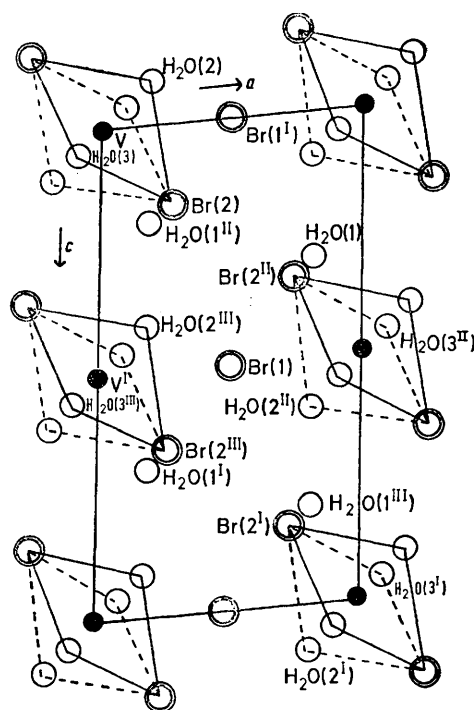


FIGURE 1. The unit cell of (I)  $[VBr_2(H_2O)_4]Br \cdot 2H_2O$  in projection down  $[010]$ . Open circles represent water molecules, closed circles vanadium atoms, and double circles bromine atoms. Roman numeral superscripts, I, II, and III, refer to symmetry-related positions for a given atom

$(0,0,0)$  and  $(0,1/2,1/2)$ . The Br-V-Br axes are inclined at *ca.*  $6^\circ$  from the perpendicular to the  $b$  axis, and make an angle of *ca.*  $60^\circ$  with the  $a$  axis. The ligand oxygens do not occupy symmetrical locations parallel to the  $(010)$  plane, but rather lie in general positions which permit the complex ion to be tilted away from the symmetrical arrangement adopted by  $[FeCl_2(H_2O)_4]^+$  ions in

<sup>5</sup> A. J. Finney, Ph.D. Thesis, University of Tasmania, 1973.

<sup>6</sup> 'International Tables for X-Ray Crystallography', vol. II, Kynoch Press, Birmingham, 1962.

$[\text{FeCl}_2(\text{H}_2\text{O})_4]\text{Cl}\cdot 2\text{H}_2\text{O}$ .<sup>7</sup> The two remaining bromide ions are fixed in a two-fold location  $(1/2, 0, 1/2)$  and  $(1/2, 1/2, 0)$ . The four oxygen atoms of the molecules of water of crystallization occupy a general  $(x, y, z)$  position located just above and below the planes with  $y = 0$  and  $y = 1/2$ .

Each bromide ion is surrounded by a distorted octahedron of six water molecules; two of these water molecules ( $\text{Br}\cdots\text{OH}_2$  3.287 Å) are not bonded to vanadium atoms, but two pairs (with  $\text{Br}\cdots\text{OH}_2$  3.273 and 3.150 Å) are bonded, one from each of four different complex ions. These four water molecules link the complex ions by hydrogen bonds to free water molecules, the  $\text{O}\cdots\text{O}$  distances being 2.644 and 2.675 Å. This possible hydrogen-bonding environment is shown in Figure 2 and some relevant distances are listed in Table 2.

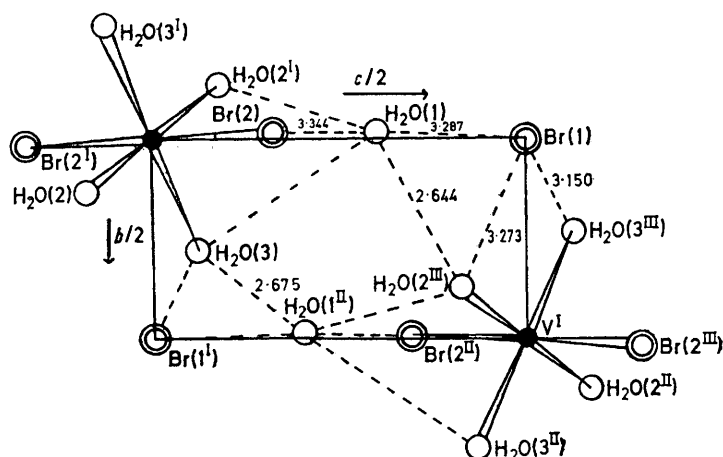


FIGURE 2 Possible hydrogen-bonding environment for (I), viewed down the  $x$  axis; distances in Å

The bromide ions lie mid-way between complex ions in the  $(010)$  plane, the closest  $\text{Br}(\text{ion})\cdots\text{Br}(\text{ligand})$  distances being 8.2 Å approximately in the plane and 6.4 Å to the complex ions centred in the plane, distant at  $y = 1/2$ . Thus the bonding between layers of complex ions in planes along the  $c$  axis is presumably both electrostatic between  $[\text{VBr}_2(\text{H}_2\text{O})_4]^+$  and  $\text{Br}^-$  ions and strengthened by hydrogen bonding as already

discussed. The compound is therefore formulated as being *trans*- $[\text{VBr}_2(\text{H}_2\text{O})_4]\text{Br}\cdot 2\text{H}_2\text{O}$ .

Similarly (II) is formulated as *trans*- $[\text{VCl}_2(\text{H}_2\text{O})_4]\text{Cl}\cdot 2\text{H}_2\text{O}$ . In the distorted octahedral unit the V-Cl bond length is 2.361 Å. The two V-OH<sub>2</sub> bond lengths (1.961 and 2.024 Å) are consistent with the corresponding bond lengths found in (I). The distortion of the complex ion from tetragonal  $D_{4h}$  symmetry is small, with bond angles deviating by less than 4° from 90°. Dimensions in the complex ion are shown in Table 2. The chloride ions Cl(2) are surrounded by a distorted octahedron of six water molecules consisting of three symmetry-related pairs with  $\text{Cl}\cdots\text{OH}_2$  3.111, 3.097, and 3.229 Å. These and other closest-approach distances in the unit cell are also given in Table 2.

The halides (I) and (II) have structures similar to that of *trans*- $[\text{FeCl}_2(\text{H}_2\text{O})_4]\text{Cl}\cdot 2\text{H}_2\text{O}$ .<sup>7</sup> The monoclinic space group adopted by (II) is  $P2_1/c$ , rather than the  $C2/m$  for the iron compound, but both have  $Z = 2$ . In the iron compound the Cl-Fe-Cl axis lies in the plane with  $y = 0$ , but the Cl-V-Cl axis is inclined at an angle of *ca.* 6° to this plane in (II). However, in the corresponding chromium compound<sup>8</sup> *trans*- $[\text{CrCl}_2(\text{H}_2\text{O})_4]\text{Cl}\cdot 2\text{H}_2\text{O}$  the Cl-Cr-Cl axis lies at an angle to the plane containing the chromium atoms, and the space group is again different, namely  $C2/c$ , with  $Z = 4$ . It is interesting that these three compounds of identical general stoichiometry, differing only in the central metal ion, should crystallize in three different monoclinic space groups.

In this context, it has also been shown recently<sup>9</sup> that  $\text{TiCl}_3\cdot 6\text{H}_2\text{O}$  has a similar powder pattern to that of  $\text{VCl}_3\cdot 6\text{H}_2\text{O}$ , both being different from the patterns obtained from  $\text{CrCl}_3\cdot 6\text{H}_2\text{O}$  and  $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$ . It can be expected, therefore, that  $\text{TiCl}_3\cdot 6\text{H}_2\text{O}$  is isomorphous with  $\text{VCl}_3\cdot 6\text{H}_2\text{O}$ . The powder data for  $\text{TiCl}_3\cdot 6\text{H}_2\text{O}$  are similar to those reported.<sup>10</sup>

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<sup>7</sup> M. D. Lind, *J. Chem. Phys.*, 1967, **47**, 990.

<sup>8</sup> I. G. Dance and H. C. Freeman, *Inorg. Chem.*, 1965, **4**, 1555.

<sup>9</sup> L. P. Podmore, Ph.D. Thesis, University of Tasmania, 1973.

<sup>10</sup> H. J. Gardiner, *Austral. J. Chem.*, 1968, **20**, 2357.