

The conformation of the *trans*-1,2-cyclohexanediaminetetraacetic acid cation is very similar to that required to give a six-coordinate octahedral or a seven-coordinate pentagonal bipyramidal coordination with a metal ion. Such geometries are very common with hexadentate ethylenediaminetetraacetate-like ligands, seven coordination being found for larger metal ions (with a monodentate ligand, usually a water molecule, occupying the seventh site) and six coordination being found for smaller metal ions (Cohen & Hoard, 1966). The two nitrogen atoms and two oxygen atoms [O(7) and O(3)] from the *pro-S* acetate groups (for the *S,S* enantiomer) are positioned to function as equatorial ligands while two oxygen atoms [O(1) and O(5)] from the *pro-R* acetate group would function as axial ligands. The overall absolute configuration for this enantiomer would be  $\Delta\Delta\Delta$  (IUPAC Commission on the Nomenclature of Inorganic Chemistry, 1970) if complexation were to occur without a large change in conformation. Others have predicted stereospecific formation of octahedral  $\Delta\Delta\Delta$  diastereomers from hexadentate (*S,S*)-1,2-cyclohexanediaminetetraacetate (Reinbold & Pearson, 1970; Erickson, Young, Ho, Watkins, Terrill & Reilly, 1971). This diastereomer is found for the six-coordinate  $\text{Mn}^{\text{III}}$  complex (Rettig & Trotter, 1973). On the other hand, the other diastereomeric pair, *R,R*( $\Delta\Delta\Delta$ ) and *S,S*( $\Delta\Delta\Delta$ ), is found for the pentagonal bipyramidal complex of  $\text{Fe}^{\text{III}}$  with an equatorial water molecule as the seventh ligand (Cohen & Hoard, 1966). Furthermore, an  $\text{Rh}^{\text{III}}$  complex, where the *trans*-1,2-cyclohexanediaminetetraacetate ligand is only tetradentate, exhibits a geometry where the ligand

is wrapping in a direction to give the unexpected isomer (Filippova, Polynova, Il'inskii, Porai-Koshits & Ezerskaya, 1981). Thus the stereoselectivity does not seem to be as great as expected.

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### Structure of *trans*-Diaquabis(oxalato)vanadate(III) Complexes: $A[\text{V}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2] \cdot x\text{H}_2\text{O}$ , $A = \text{Cs}$ ( $x = 4$ ) and $A = \text{CH}_3\text{NH}_3$ ( $x = 4.5$ )

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**Abstract.**  $\text{Cs}[\text{V}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}$  (I):  $M_r = 467.98$ , monoclinic,  $C2/m$ ,  $a = 9.256$  (4),  $b = 7.510$  (3),  $c = 10.191$  (3) Å,  $\beta = 101.79$  (7)°,  $V = 693.5$  Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 2.241$  Mg m<sup>-3</sup>,  $\text{Mo K}\alpha$ ,  $\lambda = 0.7107$  Å,  $\mu = 3.40$  mm<sup>-1</sup>,  $F(000) = 452$ , room temperature, final  $R = 0.029$  for 1077 independent reflections.

$[\text{CH}_3\text{NH}_3][\text{V}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2] \cdot 4.5\text{H}_2\text{O}$  (II):  $M_r = 376.1$ , orthorhombic,  $Cmcm$ ,  $a = 7.572$  (3),  $b = 9.251$  (4),  $c = 23.334$  (6) Å,  $V = 1634.5$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.528$  Mg m<sup>-3</sup>,  $\text{Mo K}\alpha$ ,  $\lambda = 0.7107$  Å,  $\mu = 0.66$  mm<sup>-1</sup>,  $F(000) = 780$ , room temperature, final  $R = 0.087$  for 774 independent reflections. The V atom

is octahedrally coordinated by O in both compounds, with two equivalent water molecules in axial sites [1.967 (3) Å (I); 1.955 (7) Å (II)] and with four equivalent O atoms from two coplanar oxalate groups [2.005 (2) Å (I); 2.017 (4) Å (II)]. In (II), successive molecules along [001] are rotated in opposite directions about [100], giving a doubling of the *c* axis, relative to (I). The MeNH<sub>3</sub><sup>+</sup> cation is disordered, due to wagging of the linear N—C group in the (001) plane.

Table 1. Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic thermal parameters ( $\text{Å}^2 \times 10^3$ ) with e.s.d.'s in parentheses

Compound (I)	$U_{\text{eq}} = \frac{1}{3} \text{trace } \bar{U}$			$U_{\text{eq}}$
	<i>x</i>	<i>y</i>	<i>z</i>	
Cs	0	0	0	49 (1)
V	$\frac{1}{2}$	0	$\frac{1}{2}$	23 (1)
O(1)*	3038 (3)	0	5463 (3)	47 (3)
O(2)	4282 (3)	1725 (3)	3508 (2)	32 (2)
O(3)	3137 (3)	1843 (3)	1365 (2)	52 (2)
O(4)*	3170 (4)	0	8027 (4)	56 (4)
O(5)*	720 (3)	0	3457 (3)	41 (3)
C(1)	3686 (3)	1030 (4)	2381 (3)	33 (2)
Compound (II)				
V	0	0	0	31 (1)
O(1)*	0	2044 (7)	209 (3)	51 (4)
O(2)	1716 (5)	-396 (5)	642 (2)	37 (2)
O(3)	1812 (6)	-1077 (6)	1555 (2)	57 (3)
O(4)*	0	2624 (9)	1303 (3)	59 (5)
O(5)*	0	3917 (8)	-635 (4)	53 (4)
O(6)*†	1494 (52)	1416 (40)	$\frac{1}{2}$	69 (21)
N	0	-2546 (15)	$\frac{1}{4}$	62 (9)
C(1)	1017 (8)	-760 (7)	1122 (3)	39 (4)
C(2)†	1236 (100)	-3774 (45)	$\frac{1}{4}$	220 (70)

\* Water O atoms.

† Site occupancy of C(2), O(6) = 0.50, 0.25 respectively.

Table 2. Relevant bond lengths (Å) and bond angles (°) for (I) and (II)

	(I)	(II)
V—O(1)	1.967 (3)	1.955 (7)
V—O(2)	2.005 (2)	2.017 (4)
O(2)—O(2)	2.591 (4)	2.599 (8)
O(1)—O(2)	2.805 (4)	2.822 (8)
O(1)—O(2)	2.812 (4)	2.797 (8)
O(2)—O(3)	2.226 (3)	2.220 (7)
O(3)—O(3)	2.768 (5)	2.744 (10)
C(1)—C(1)	1.547 (6)	1.542 (12)
C(1)—O(2)	1.280 (3)	1.281 (8)
C(1)—O(3)	1.220 (3)	1.212 (8)
O(1)—O(4)	2.592 (5)	2.606 (11)
O(1)—O(5)	2.644 (4)	2.622 (11)
O(2)—O(5)	2.802 (4)	2.838 (8)
O(3)—O(4)	2.788 (5)	2.758 (10)
Cs—O(5)	3.449 (3)	
Cs—O(3)	3.260 (3)	
Cs—O(3)	3.393 (3)	
Cs—O(4)	3.881 (4)	
O(1)—V—O(2)	90.1 (1)	89.5 (2)
O(2)—V—O(2)	80.5 (5)	80.2 (2)
C(1)—O(2)—V	115.6 (2)	115.5 (4)
O(2)—C(1)—O(3)	125.9 (3)	125.9 (6)
C(1)—C(1)—O(3)	120.0 (3)	119.7 (6)
C(1)—C(1)—O(2)	114.1 (3)	114.4 (7)

**Introduction.** As part of a general study of the structures and properties of vanadium(III) aqua-complexes (Podmore & Smith, 1972; Donovan & Smith, 1975; Donovan, Podmore & Smith, 1976) the diaquabis(oxalato) complexes (I) and (II) were prepared. We report here the X-ray structure analysis of both compounds.

**Experimental.** (I) and (II) were prepared by treating a solution of VCl<sub>3</sub>.6H<sub>2</sub>O with oxalic acid and adding an aqueous solution of CsCl or MeNH<sub>3</sub>Cl. Red-purple lozenge-shaped crystals formed on cooling the solutions to 273 K.  $D_m$  not measured. Cell parameters determined from Weissenberg and precession photographs, on crystals 0.12 × 0.20 × 0.30 mm (I) and 0.20 × 0.20 × 0.22 mm (II), and refined on a Siemens AED single-crystal diffractometer using 15 carefully centred high-angle ( $15 < \theta < 25^\circ$ ) reflections;  $\theta$ - $2\theta$  scan,  $2\theta$  range 5–60° (I), 5–50° (II); total of 2184 reflections measured for  $h = -12$  to 12,  $k = 0$  to 10,  $l = -14$  to 14 (I) and 2851 reflections for  $h = -8$  to 8,  $k = 0$  to 10,  $l = -27$  to 27 (II); one standard reflection measured every 3 h, less than 3% intensity variation; data corrected for absorption, transmission coefficients: max. 0.68, min. 0.51 (I) and 0.89, 0.86 (II); 1077 (I), 744 (II) unique reflections used in structure refinement;  $R_{\text{int}}$  0.012 (I), 0.027 (II); structure solved by heavy-atom and Fourier methods and refined on  $F$  by full-matrix anisotropic least squares to final  $R$  0.029 (I) and 0.087 (II); all H atoms located in difference Fourier map for (I), only those associated with the bonded water found for (II); unit weights; 54 (I) and 64 (II) parameters refined; max.  $\Delta/\sigma$  0.01 (I) and 0.13 (II); largest peak in final difference map 0.46 e Å<sup>-3</sup> (I) and 0.61 e Å<sup>-3</sup> (II); no correction for secondary extinction; scattering factors from *International Tables for X-ray Crystallography* (1974); programs: *SHELX76* (Sheldrick, 1976) and *ORTEP* (Johnson, 1965).

**Discussion.** Atomic coordinates are given in Table 1.\* Bond lengths and angles of interest are given in Table 2. A perspective view of the [V(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]<sup>-</sup> complex is shown in Fig. 1. There is very little variation in the geometry of the complex with change of cation, all bond lengths and angles agreeing to within two combined standard deviations. The V is octahedrally coordinated to four coplanar O atoms from the oxalate ligands and two water molecules. The V—O(1)H<sub>2</sub> axial bonds are perpendicular to the plane of the oxalate ligands, and are significantly shorter than the equatorial

\* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39947 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

V—O(2) bonds, the V—O(1)/V—O(2) ratio being 0.981 for (I) and 0.969 for (II). It is interesting to compare the results in Table 2 with those for the compound  $K[Cr(C_2O_4)_2(H_2O)_2] \cdot 3H_2O$  which contains the same type of octahedral *trans*-diaquabis(oxalato)metal(III) complex anion (van Niekerk & Schoening, 1951). In contrast with the V compounds, the axial Cr—OH<sub>2</sub> bonds are *longer* than the equatorial bonds; Cr—O(axial)/Cr—O(equatorial) = 1.05. The difference may be explained in terms of stronger H bonding of the protons associated with the axial H<sub>2</sub>O molecules in the V compounds (*i.e.* higher polarization of the O), and also in terms of the different cation packings, that result in cation—OH<sub>2</sub> (axial) ionic bonds for the Cr compound (K—OH<sub>2</sub> = 3.1 Å) but not for the V compounds (shortest Cs—OH<sub>2</sub> is >5.5 Å).

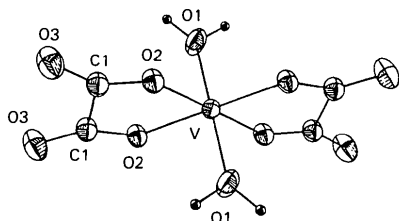


Fig. 1. Structure of the complex anion, showing atom labelling and 50% probability ellipsoids.

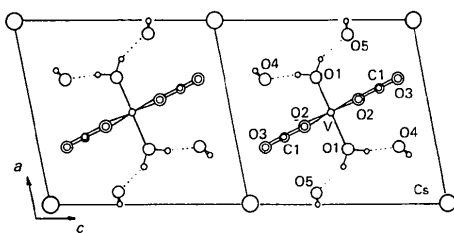


Fig. 2. A (010) slice through the structure of (I) from  $y = -\frac{1}{4}$  to  $y = \frac{1}{4}$ . Atoms lying above and below the mirror plane at  $y = 0$  are shown by double circles.

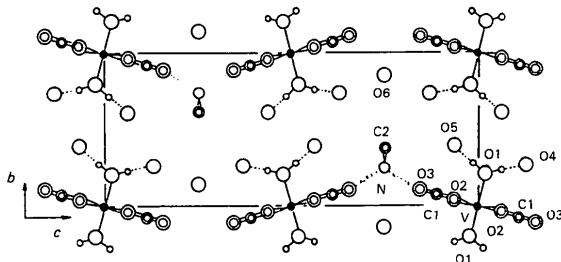


Fig. 3. A (100) slice through the structure of (II) from  $x = -\frac{1}{4}$  to  $x = \frac{1}{4}$ . Atoms lying above and below the mirror plane at  $x = 0$  are shown by double circles.

Sections of the structures of (I) and (II) perpendicular to the 7.5 Å axis are shown in Figs. 2 and 3. The H bonding determined for the Cs compound is shown in Fig. 2. Strong H bonding within the (010) plane occurs between the bonded water molecule, H<sub>2</sub>O(1), and the isolated water molecules H<sub>2</sub>O(4) and H<sub>2</sub>O(5). Weaker H bonding also occurs between these two molecules and oxygens O(2) and O(3) of oxalate groups in (010) planes above and below that shown in Fig. 2.

In the Cs compound, the complex anions all have the same orientation, with the O(1)—V—O(1) axial bonds lying perpendicular to **b** and making an angle of 13.5 (1)° with **a** (9.25 Å), whereas in the methylammonium compound, successive complex anions along **c** are rotated in opposite senses about **a** so that the O(1)—V—O(1) bonds make angles of ±14.5 (1)° with **b** (9.25 Å). The location of the isolated water molecules H<sub>2</sub>O(4) and H<sub>2</sub>O(5) in relation to the complex anion is very similar in (I) and (II) [compare the distances O(1),O(2)—O(4),O(5) in Table 2], but the cations occupy different relative positions. The methylammonium cation is disordered; the —NH<sub>3</sub> groups are pinned to fixed positions in the (100) plane, Fig. 3, presumably due to strong bonding to the terminal oxygens, O(3), of pairs of adjacent oxalate ligands, whereas the —CH<sub>3</sub> group is disordered between two positions, located 0.94 Å above and below the (100) plane. A difference Fourier map showed a continuous arc of residual intensity between these two positions, suggesting that the disorder may be dynamic, due to wagging in the (001) mirror planes. A partially occupied water site [H<sub>2</sub>O(6)] was also located in the (001) mirror plane, at a distance of 2.82 Å from the methyl C. There were no corresponding partially occupied sites in the Cs compound. The Cs is bonded to ten O atoms in the range 3.260–3.449 Å, with a further two, O(4), at 3.881 Å.

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