Discussion. Interatomic distances and angles are given in Table 2. The structural arrangement is in agreement with previous work (Gottfried & Schusterius, 1933; Mani, 1957). However, the precision in the present work is better by more than one order of magnitude. The Cl–O distances [mean 1·433 (2) Å] compare well with values found in six recent investigations (Berglund, Thomas & Tellgren, 1975).

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Caesium Triaquabis(oxalato)titanate(III) Dihydrate

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Abstract. $Cs[Ti(C_2O_4)_2(H_2O)_3].2H_2O$, $C_4H_{10}CsTiO_3$, M_r = 446·92, monoclinic, a = 6·543 (8), b = 11·490 (11), c = 8·015 (9) Å, β = 96·51 (8)°, U = 598·7 Å^3, Z = 2, d_m = 2·54 (3), d_c = 2·48 g cm^{-3}, Mo $K\alpha$ radiation, λ = 0·7107 Å, μ = 39·0 cm^{-1}, space group $P2_1/m$ (from systematic absences $0k0$, $k = 2n + 1$ and the successful structure determination). The anion has crystallographically imposed C_s symmetry. The Ti atom is in a seven-coordinate pentagonal-bipyramidal environment with two water molecules in axial sites [2·101 (5), 2·070 (5) Å], and one in the equatorial girdle [2·130 (5) Å] together with both oxalates [2·314 (5), 2·115 (3) Å]. 1510 independent reflexions collected by counter methods have been refined to R = 0·042.

Introduction. $Cs[Ti(ox)_2(H_2O)_3].2H_2O$ (ox = oxalate) was prepared by adding 0·5 g $TiCl_3$ to a hot solution of 0·7 g of oxalic acid hydrate in 20 cm^3 water and subsequently adding a solution of 0·6 g of Cs carbonate and 0·5 g oxalic acid in 10 cm^3 water. Reactions were carried out under nitrogen. Crystals of a lower hydrate, possibly $Cs[Ti(ox)_2(H_2O)_2]$, were first formed as fine gold/orange plates but these recrystallized after several hours to form much coarser brown crystals of the title compound. A crystal with dimensions *ca* 0·25 × 0·3 × 0·4 mm was mounted with the a^* axis parallel to the instrument axis of a GE XRD 5 apparatus, which was used to measure cell dimensions *via* least-squares refinement of high-angle reflexions and diffraction intensities by the stationary-crystal–stationary-counter method. It was equipped with a manual goniostat, a scintillation counter and a pulse-height discriminator. Zr-filtered Mo radiation was used with a 4° take-off angle and a counting time of 10 s. 1830 independent reflexions were measured with $2\theta < 60°$ and, of these, 1510 with $I > 3\sigma(I)$ were used in subsequent calculations. An absorption correction was applied using the *ABSORB* program (Stewart, Kruger, Ammon, Dickinson & Hall, 1972). The positions of the Cs atoms were obtained from a Patterson function and the positions of the Ti, C and O atoms from a Fourier map. After these atoms were refined anisotropically *via* full-matrix least squares, a difference Fourier map was calculated and the positions of four of the five independent H atoms were located. These were included in the refinement and given isotropic thermal parameters. The final R value was 0·042. In the final cycle no shift was >0·01σ. The weighting scheme, chosen to give constant values of $w\Delta^2$ over ranges of F_o and sin θ/λ, was $\sqrt{w} = 1$ for $F_o < 12·5$ and $12·5/F_o$ for $F_o > 12·5$. Calculations were performed on a CDC 7600 computer at the University of London Computer Centre with the XRAY system (Stewart *et al.*, 1972).

Atomic scattering factors for all atoms were taken from *International Tables for X-ray Crystallography* (1974), as were the corrections for the real and imaginary part of the anomalous dispersion for Cs and Ti. The anisotropic thermal parameter is defined as $\exp(-2\pi^2 \times \Sigma_i \Sigma_j h_i h_j U_{ij} b_i b_j)$ (i,j = 1,2,3), with b_i the ith reciprocal-lattice dimension, and the isotropic thermal parameter as $\exp(-8\pi^2 U \sin^2\theta/\lambda^2)$. Final positional coordinates are given in Table 1, bond lengths and angles in the anion in Table 2.*

Table 1. *Positional parameters* ($\times 10^4$ *for* Ti, Cs, C, O; $\times 10^3$ *for* H) *with estimated standard deviations in parentheses*

	x	y	z
Cs	515 (1)	2500*	−2861 (1)
Ti	6578 (1)	7500*	7711 (1)
O(1)	3672 (7)	7500*	6296 (6)
O(2)	9588 (7)	7500*	8832 (6)
O(3)	5295 (8)	7500*	10037 (6)
O(4)	6242 (5)	5754 (3)	8545 (4)
O(5)	7502 (5)	6409 (3)	5808 (4)
O(6)	6446 (7)	3865 (3)	7882 (5)
O(7)	7576 (6)	4603 (3)	4805 (4)
O(8)	1266 (6)	5357 (4)	8422 (4)
C(1)	6594 (6)	4914 (3)	7575 (5)
C(2)	7280 (6)	5317 (3)	5908 (5)
H(1)	368 (12)	678 (7)	583 (9)
H(2)	1014 (11)	699 (6)	878 (9)
H(3)	462 (12)	683 (7)	1056 (9)
H(81)	167 (10)	528 (6)	738 (8)
H(82)	240*	525*	900*

* Parameter fixed.

Table 2. *Final molecular dimensions with estimated standard deviations in parentheses* (*in* Å *and degrees*)

Ti–O(1)	2·101 (5)	O(4)–C(1)	1·277 (5)
Ti–O(2)	2·070 (5)	O(5)–C(2)	1·266 (5)
Ti–O(3)	2·130 (5)	C(1)–O(6)	1·236 (5)
Ti–O(4)	2·134 (3)	C(2)–O(7)	1·237 (5)
Ti–O(5)	2·115 (3)	C(1)–C(2)	1·529 (6)
O(1)–Ti–O(2)	173·2 (2)	O(4)–Ti–O(4$^{\rm i}$)	140·2 (1)
O(1)–Ti–O(3)	92·9 (2)	O(4)–Ti–O(5$^{\rm i}$)	146·2 (1)
O(1)–Ti–O(4)	92·9 (1)	O(5)–Ti–O(5$^{\rm i}$)	72·7 (1)
O(1)–Ti–O(5)	85·7 (1)		
O(2)–Ti–O(3)	94·0 (2)	O(4)–C(1)–O(6)	126·3 (4)
O(2)–Ti–O(4)	89·5 (1)	O(4)–C(1)–C(2)	113·2 (3)
O(2)–Ti–O(5)	88·7 (1)	O(6)–C(1)–C(2)	120·4 (4)
O(3)–Ti–O(4)	70·2 (1)	O(5)–C(2)–O(7)	125·7 (4)
O(3)–Ti–O(5)	143·6 (1)	O(5)–C(2)–C(1)	113·7 (4)
O(4)–Ti–O(5)	73·5 (1)	O(7)–C(2)–C(1)	120·6 (4)
O(1)–H(1)	0·91 (8)	Ti–O(1)–H(1)	100 (5)
O(2)–H(2)	0·68 (7)	Ti–O(2)–H(2)	117 (6)
O(3)–H(3)	1·00 (8)	Ti–O(3)–H(3)	127 (4)
O(8)–H(81)	0·91 (7)	H(1)–O(1)–H(1$^{\rm i}$)	131 (7)
O(8)–H(82)	0·84*	H(2)–O(2)–H(2$^{\rm i}$)	116 (9)
		H(3)–O(3)–H(3$^{\rm i}$)	100 (6)

* Parameter fixed.

Discussion. The analysis of the title compound was carried out as part of our studies on the oxalates of titanium(III). Previous work includes the preparation of M'[Ti(ox)$_2$].2H$_2$O (M' = K,NH$_4$) (Eve & Fowles, 1966) and the crystal structure determination of Ti$_2$(ox)$_3$.10H$_2$O (Drew, Fowles & Lewis, 1969) in which a centrosymmetric dimer, Ti$_2$(ox)$_3$(H$_2$O)$_6$, is found. Each metal atom is in a seven-coordinate pentagonal-bipyramidal environment with two water

Table 3. *Intermolecular contacts*

Distances are in Å, angles in degrees.

(*a*) Details of hydrogen-bonding scheme

O(1)···O(7$^{\rm ii}$)	2·669	H(1)···O(7$^{\rm ii}$)···H(81)	88
O(1)–H(1)···O(7$^{\rm ii}$)	152	H(1)···O(7$^{\rm ii}$)–C(2$^{\rm ii}$)	132
O(2)···O(8$^{\rm iii}$)	2·731	H(81)···O(7$^{\rm ii}$)–C(2$^{\rm ii}$)	134
O(2)–H(2)···O(8$^{\rm iii}$)	169	H(2$^{\rm v}$)···O(8)–H(81)	111
O(3)···O(6$^{\rm iv}$)	2·640	H(2$^{\rm v}$)···O(8)–H(82)	112
O(3)–H(3)···O(6$^{\rm iv}$)	155	H(81)–O(8)–H(82)	99
O(8)···O(4$^{\rm iv}$)	3·049	H(3)···O(6$^{\rm iv}$)–C(2$^{\rm iv}$)	132
O(8)–H(82)···O(4$^{\rm iv}$)	139	H(82)···O(4$^{\rm iv}$)–C(1$^{\rm iv}$)	94
O(8)···O(7$^{\rm ii}$)	2·777		
O(8)–H(81)···O(7$^{\rm ii}$)	170		

(*b*) Cs coordination

Cs···O(8$^{\rm vi,xi}$)	3·459	Cs···O(3$^{\rm ii}$)	3·351
Cs···O(6$^{\rm vii,x}$)	3·204	Cs···O(5$^{\rm viii}$)	3·087
Cs···O(7$^{\rm vii,x}$)	3·496	Cs···O(1$^{\rm xiv}$)	3·658
Cs···O(2$^{\rm ii,ix}$)	3·237		

(*c*) Other contacts (not involving hydrogen) less than 3·50 Å

O(5)···O(8$^{\rm iii}$)	3·278	C(1)···O(8$^{\rm iv}$)	3·366
C(1)···O(8$^{\rm iii}$)	3·100	O(7)···O(4$^{\rm ii}$)	3·478
C(2)···O(8$^{\rm iii}$)	3·110	C(1)···O(7$^{\rm ii}$)	3·195
O(4)···O(8$^{\rm iii}$)	3·331	C(2)···O(7$^{\rm ii}$)	3·166
O(4)···O(8)	3·278	C(2)···C(2$^{\rm ii}$)	3·251
O(7)···O(7$^{\rm xii}$)	3·281	O(8)···O(8$^{\rm xiii}$)	3·282
O(7)···C(2$^{\rm xii}$)	3·478		
O(4)···O(4$^{\rm iv}$)	3·456		
O(8)···O(6$^{\rm iv}$)	3·288		

Superscripts refer to the following equivalent positions with respect to the set at x,y,z (Table 1):

(i)	$x, 1\frac{1}{2}-y, z$	(viii)	$1-x, 1-y, -z$
(ii)	$1-x, 1-y, 1-z$	(ix)	$1-x, -\frac{1}{2}+y, 1-z$
(iii)	$1+x, y, z$	(x)	$-1+x, \frac{1}{2}-y, -1+z$
(iv)	$1-x, 1-y, 2-z$	(xi)	$x, \frac{1}{2}-y, -1+z$
(v)	$-1+x, y, z$	(xii)	$2-x, 1-y, 1-z$
(vi)	$x, y, -1+z$	(xiii)	$-x, 1-y, 2-z$
(vii)	$-1+x, y, -1+z$	(xiv)	$-x, 1-y, -z$

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32685 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

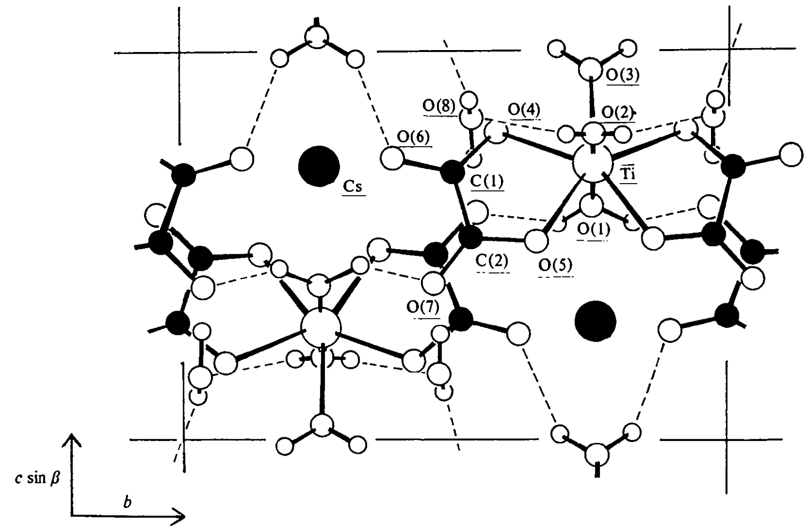

Fig. 1. The structure of $Cs[Ti(ox)_2(H_2O)_3].2H_2O$ in the *a* projection (open circles: large Ti, medium O, small H; closed circles: large Cs, medium C).

molecules in axial positions and one in an equatorial plane, together with one bridging and one non-bridging oxalate ligand.

The structure of the Cs complex is shown in Fig. 1. In the discrete anion, which has crystallographically imposed C_s symmetry, the metal atom is also seven-coordinate with a pentagonal-bipyramidal environment. This is the expected geometry for seven-coordinate complexes of the form $ML_3(L-L)_2$ ($L, L-L$ being monodentate and bidentate ligands) (Drew, 1977). Two water molecules occupy axial positions [2·101 (5), 2·070 (5) Å], and a water molecule [2·130 (5) Å] together with two bidentate oxalate ligands [2·134 (3), 2·115 (3) Å] are in equatorial positions. The bonds to the axial atoms are shorter than those to the equatorial atoms; this difference is a common feature of pentagonal-bipyramidal structures (Drew, 1977).

The Ti–O(ox) bond lengths [2·134 (3), 2·115 (3) Å] are shorter than the bridging bonds [2·16 (1), 2·19 (1) Å] and longer than the non-bridging bonds [2·09 (1), 2·08 (1) Å] in the dimer. The angle subtended at the metal by the oxalate is 73·5 (1)°, ideally suited to the pentagonal girdle, and there is very little distortion from D_{5h} symmetry in the MO_7 coordination sphere. No O_{ax}–Ti–O_{eq} angle is more than 4·3° from 90°. The maximum deviation of a contributing atom from the TiO_5 girdle plane is 0·06 Å. As is usually the case for a non-bridging oxalate, the bonds from C to the non-bonded O atoms are significantly shorter than the others (mean 1·271 *vs* 1·237 Å). The oxalate ligand is slightly buckled with a maximum deviation of a contributing atom from the C_2O_4 plane of 0·04 Å. The metal atom is 0·13 Å from this plane.

There are some very close contacts between O atoms and these form the basis for a hydrogen-bond scheme outlined in Table 3 and illustrated in Fig. 1. The Cs atom has eleven O atoms in the inner coordination sphere (3·09–3·66 Å). Other intermolecular contacts are shown in Table 3.

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