Inorganica Chimica Acta, *193* (1992) 99–103

Crystal structure of cesium–bis(oxalato)oxo–titanate(IV) hydrate

A. Fester, W. Bensch and M. Trömel

Institut für Anorganische Chemie der Universität Frankfurt am Main, Niederurseler Hang, W 6000 Frankfurt/Main 50 (FRG)

(Received September 9, 1991; revised November 5, 1991)

Abstract

The crystal structure of cesium–bis(oxalato)oxo–titanate(IV) hydrate $Cs_4[TiO(C_2O_4)_2]_2 \cdot 3H_2O$ was determined from X-ray diffraction studies and refined by least-squares methods to $R = 0.032$ using 3831 reflections. The compound crystallizes in the triclinic space group $P\bar{1}$ with one tetranuclear anion in the unit cell. The lattice parameters are $a = 1090.4(6)$, $b = 1156.8(7)$, $c = 1161.9(8)$ pm, $\alpha = 63.84(2)$, $\beta = 75.88(2)$, $\gamma = 64.39(2)°$ and $V = 1.193 \times 10^9$ pm^3. The tetranuclear anions form eight-membered rings composed of four titanium and four oxygen atoms. The titanium atoms are in a distorted octahedral environment. The distances between Ti and O in the non-planar ring with an inversion centre range from 182.9 to 179.6 pm. The arrangement of the rings leads to holes of up to 600 pm in diameter. Cesium atoms as well as the crystal water are located in these holes. The cesium ions show a nine-, ten- or twelve-fold surrounding. Typical bond lengths to oxygen are between 292 and 372 pm. The crystal water molecules are slightly disordered.

Introduction

In contrast to well known ions like VO^{2+} or VO^{3+} corresponding ions of titanium(IV) with a (Ti=O) double bond have not been found until now. The very rare investigations of so called 'titanyl' compounds all show chain or ring systems.

Examples of more organic type compounds with tetrameric or dimeric structures are alkoxides like $Ti(OC_2H_5)_4$ [1] or the β-diketonate $[TiO(C_5H_7O_2)_2]_2$ [2]. (Ti–O) chains are found in inorganic compounds like $TiOSO_4$ [3] or $KTiOPO_4$ [4]. An eight-membered ring is observed in $(NH_4)_2TiO(C_2O_4)_2 \cdot H_2O$ [5, 6]. The only well characterized compound with a short (Ti–O) bond of 161.9 pm is a titanyl porphyrin [7]. $(NH_4)_2[VO(C_2O_4)_2(H_2O)] \cdot H_2O$ [8] is a monomeric analogue to $(NH_4)_2TiO(C_2O_4)_2 \cdot H_2O$ with a ring system and it was of interest to find whether other titanyl compounds of this composition show comparable structures. Preliminary studies of alkaline salts of titanium(IV) complexes [9] suggested the existence of cyclic structures. In order to obtain more information about these compounds $Cs_4[TiO(C_2O_4)_2]_2 \cdot 3H_2O$ was prepared and the single crystal structure was determined.

Experimental

The preparation of $Cs_4[TiO(C_2O_4)_2]_2 \cdot 3H_2O$ starts with the synthesis of a 0.5 M solution of $TiCl_4$ in water. It is prepared by dissolving freshly precipitated $Ti(OH)_4$ in the calculated amount of HCl. Afterwards two equivalents of oxalic acid were added carefully. After cooling with ice, 3–4 equivalents of CsOH are added slowly while stirring. This process takes up to 5 h to avoid the precipitation of $Ti(OH)_4$. The pH of the solution at the end of this procedure is about 1–2. Within a day half the volume of ethanol is added carefully to get two slightly mixed layers. After a few days colourless crystals of $Cs_4[TiO(C_2O_4)_2]_2 \cdot 3H_2O$ can be isolated in a yield of 85%.

Anal. Found: Cs, 49.6; Ti, 8.8; $(C_2O_4)^{2-}$, 33.4; H_2O, 5.5. Calc. for $Cs_4[TiO(C_2O_4)_2]_2 \cdot 3H_2O$: Cs, 49.9; Ti, 9.0; $(C_2O_4)^{2-}$, 33.0; H_2O, 5.1%. A crystal of dimensions $0.3 \times 0.3 \times 0.5$ mm was chosen for preliminary Weissenberg photographs to check the quality of the crystal and to determine the unit cell. They indicated the crystal system to be triclinic.

Data collection and reduction

The X-ray diffraction intensity data were collected on a Stoe AED II four-circle diffractometer at room temperature, ω-scan technique, using a graphite monochromator (Mo Kα radiation, $\lambda = 0.7107$ Å, scintillation counter). A total of 4173 unique reflections was collected in the range of 3–50° in 2θ with indices h: -12 to 12, k: -13 to 13 and l: -3 to 13. The calculated density of 2.85 g cm^{-3} agreed well with the observed value of 2.81 g cm^{-3} measured by flotation. This leads to two formula units in the unit cell. The intensity data were reduced to structure factors by Lorentz and polarization

0020-1693/92/$5.00 © 1992 – Elsevier Sequoia. All rights reserved

corrections. An empirical absorption correction was applied with a range of transmission factors between 0.484 and 0.939. The statistical distribution of normalized structure factors suggested a center of symmetry. Therefore, the space group $P\bar{1}$ was adopted for the calculations.

Structure determination and refinement

The structure was solved by direct methods, using the SHELX TL plus program system [10]. Atomic scattering factors for Cs, Ti, O, C and H were taken from the International Tables [11]. All non-hydrogen atoms could be located in difference syntheses. The full-matrix least-squares refinement with anisotropic temperature factors resulted in the final R values $R = 0.0320$ and $R_w = 0.0344$. The weighting scheme $w = 1/(\sigma^2(F) + 0.00005F^2)$ shows no significant dependences on sin θ/λ and $F_0/F_{0\ \max}$. An extinction correction was applied with $g = 0.00080(6)$ in $F^* = F_c/(1 + 0.002gF_c^2/\sin 2\theta)^{1/4}$.

TABLE 1. Atomic parameters of $Cs_4[TiO(C_2O_4)_2]_2 \cdot 3H_2O$

	x	y	z	B_{eq} (Å^2)
Cs1	0.14426(4)	0.92235(4)	0.20048(4)	2.97(2)
Cs2	0.38925(4)	0.19456(5)	0.06211(4)	3.22(2)
Cs3	0.23081(4)	0.71538(5)	0.83093(4)	3.11(2)
Cs4	0.27809(4)	0.53442(5)	0.55959(4)	3.23(2)
Ti1	0.12418(10)	0.53327(10)	0.28406(9)	1.75(5)
Ti2	0.13019(10)	0.24059(10)	0.57187(9)	1.76(5)
O1	0.1580(4)	0.3881(4)	0.4354(4)	2.7(2)
O2	−0.0172(4)	0.3329(5)	0.6523(4)	2.7(2)
O3	−0.0160(4)	0.4848(4)	0.2537(4)	2.3(2)
O4	0.0644(5)	0.6818(5)	0.1019(4)	2.7(2)
O5	−0.1789(5)	0.5488(6)	0.1296(5)	4.2(3)
O6	−0.0908(5)	0.7670(6)	−0.0384(5)	4.3(3)
O7	0.2727(4)	0.4244(5)	0.1838(5)	3.3(3)
O8	0.2807(4)	0.5907(5)	0.2652(4)	2.6(2)
O9	0.5004(7)	0.5492(11)	0.2062(10)	10.3(8)
O10	0.4887(7)	0.3683(14)	0.1129(13)	15.9(9)
O11	0.1593(4)	0.0552(4)	0.7339(4)	2.7(2)
O12	0.2774(4)	0.2269(4)	0.6595(4)	2.5(2)
O13	0.2581(6)	−0.0693(5)	0.9201(4)	3.9(3)
O14	0.3964(5)	0.1125(5)	0.8329(5)	3.7(3)
O15	0.0039(4)	0.2054(4)	0.5043(4)	2.5(2)
O16	0.2634(4)	0.1107(5)	0.4776(4)	2.9(2)
O17	−0.0164(6)	0.1290(6)	0.3659(5)	4.3(3)
O18	0.2712(6)	0.0256(7)	0.3362(6)	5.1(3)
O19	0.4418(9)	−0.2660(10)	0.3130(13)	11.1(8)
O20	0.5271(11)	0.1223(12)	0.3603(11)	12.1(8)
O21	0.5553(10)	−0.7075(13)	0.4526(14)	13.6(9)
C1	−0.0829(6)	0.5632(7)	0.1518(6)	2.4(3)
C2	−0.0357(6)	0.6833(7)	0.0611(6)	2.6(3)
C3	0.3903(8)	0.4303(14)	0.1673(13)	7.2(8)
C4	0.3954(8)	0.5314(11)	0.2153(10)	5.2(6)
C5	0.2374(6)	0.0278(6)	0.8161(6)	2.4(3)
C6	0.3123(6)	0.1290(6)	0.7690(6)	2.5(3)
C7	0.0530(7)	0.1414(7)	0.4243(6)	2.7(3)
C8	0.2093(7)	0.0862(7)	0.4088(6)	3.2(4)

TABLE 2. Bond lengths and angles in the titanium–oxygen octahedrons

Ti1–O1	1.796(4)	Ti2–O1	1.829(4)
Ti1–O2	1.825(5)	Ti2–O2	1.806(4)
Ti1–O3	1.988(6)	Ti2–O11	2.095(4)
Ti1–O4	2.087(4)	Ti2–O12	2.018(6)
Ti1–O7	2.044(5)	Ti2–O15	1.993(6)
Ti1–O8	2.018(6)	Ti2–O16	2.087(4)
Ti1–O1–Ti2	156.2(1)	Ti2–O2–Ti1	157.1(1)
O1–Ti1–O2	97.3(1)	O2–Ti2–O1	99.5(1)
O1–Ti1–O3	91.3(1)	O2–Ti2–O15	87.6(1)
O1–Ti1–O8	168.4(1)	O2–Ti2–O16	164.0(1)
O1–Ti1–O7	93.7(1)	O2–Ti2–O11	91.0(1)
O1–Ti1–O4	99.8(1)	O2–Ti2–O12	98.9(1)
O2–Ti1–O4	100.9(1)	O1–Ti2–O15	102.1(1)
O2–Ti1–O7	87.7(1)	O1–Ti2–O11	88.9(1)
O2–Ti1–O3	162.8(1)	O1–Ti2–O16	163.0(1)
O2–Ti1–O8	88.1(1)	O1–Ti2–O12	88.5(1)
O3–Ti1–O4	77.4(1)	O15–Ti2–O16	77.3(1)
O4–Ti1–O8	92.0(1)	O15–Ti2–O11	91.5(1)
O4–Ti1–O7	164.8(1)	O15–Ti2–O12	166.5(1)
O3–Ti1–O7	84.0(1)	O16–Ti2–O11	84.2(1)
O3–Ti1–O8	90.8(1)	O16–Ti2–O12	94.8(1)
O7–Ti1–O8	77.0(1)	O11–Ti2–O12	76.6(1)

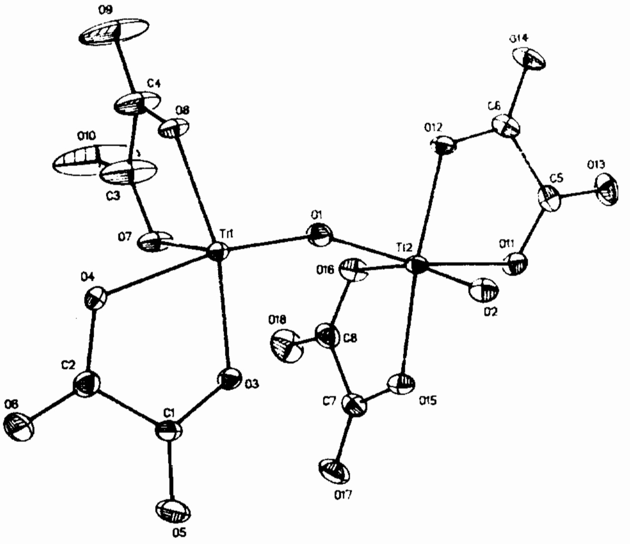

Fig. 1. Asymmetric unit of the anion in $Cs_4[TiO(C_2O_4)_2]_2 \cdot 3H_2O$.

In the final stages 3831 reflections were used with $I > 2\sigma(I)$. The final difference Fourier synthesis did not show any significant peaks higher than 1.2 e/Å^2. The positional and isotropic thermal parameters are listed in Table 1. See also 'Supplementary material'.

Results and discussion

Important bond angles and distances are summarized in Table 2. The consecutive numbering of the atoms corresponds to Fig. 1. In contrast to a first assumption

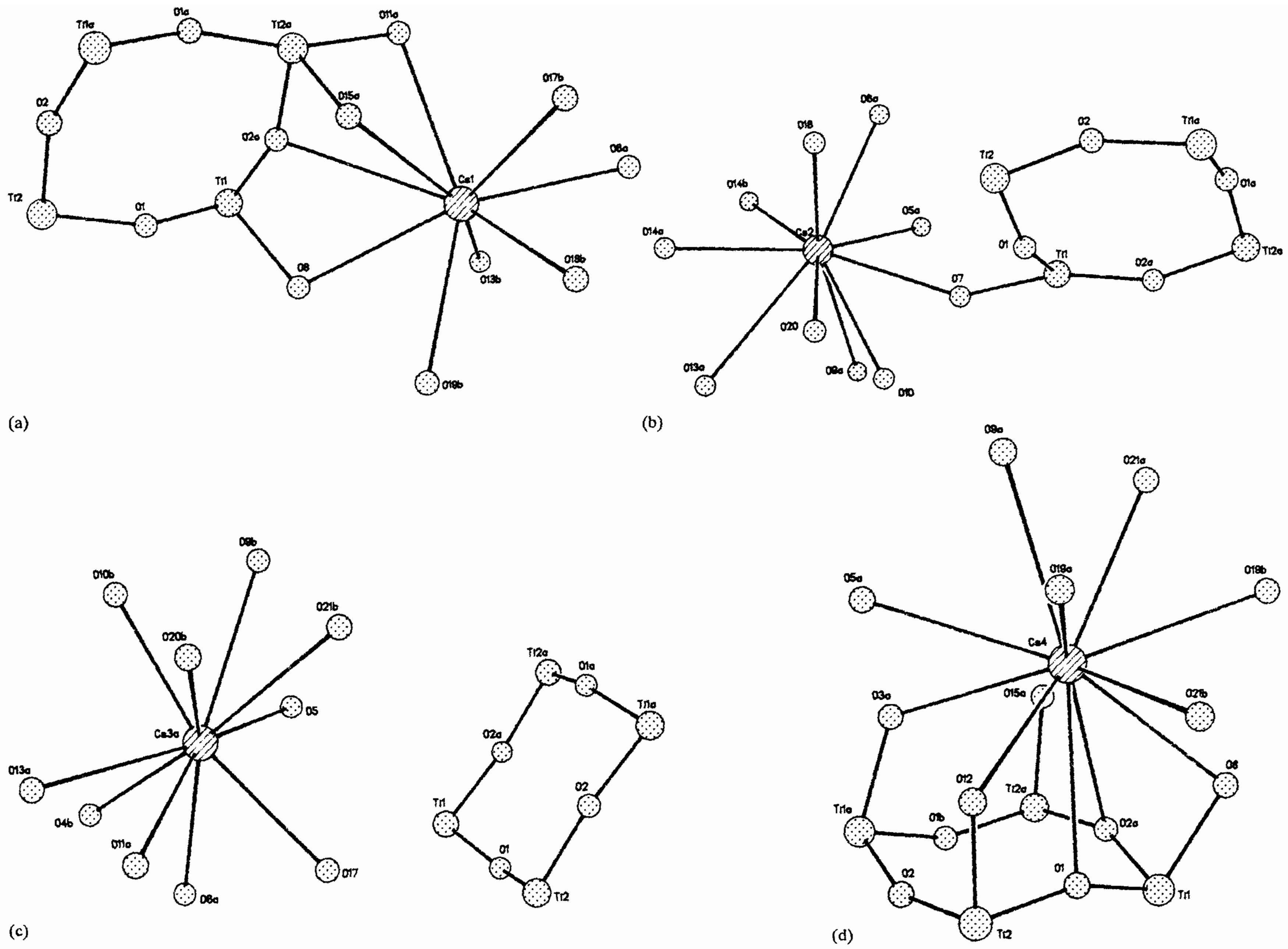

Fig. 2. Coordination sphere of: (a) Cs1, (b) Cs2, (c) Cs3, (d) Cs4.

[12] the structure consists of $(TiO)_4$ rings in which titanium is in a distorted octahedral coordination. The tetrameric anion is shown in Fig. 1. The observed structure with the eight-membered ring is comparable with the ring system found in $(NH_4)_2TiO(C_2O_4)_2 \cdot H_2O$. The octahedra share apices, and bond angles as well as interatomic distances are very similar. The (Ti–O) bonds of 179.6 to 182.9 pm within the ring system are significantly shorter than those to the oxalate oxygen (about 200 pm). The expected distance for a (Ti–O) single bond is 181 pm [13, 14].

The strong distortion of the octahedral coordination around titanium can be seen in Table 2. The angles deviate significantly from the expected values of 90 and 180°. They vary from 76.6 to 102.4° and the 180° angles are about 15° too low. The atoms O19–O21 are oxygens of the crystal water. As can been seen in Table 1 the thermal parameters are relatively high, due to a slight disorder. A small disorder is also observed for one of the oxalate groups (C3, C4, O9 and O10). The water molecules are coordinated to cesium with distances ranging from 322 to 372 pm. The distances to titanium are larger than 460 pm and those of the oxygen atoms of the oxalate groups are of the same order. Therefore, hydrogen bonding between the water molecules and the oxalate oxygen atoms can be excluded.

As is well known from other cesium compounds the coordination sphere around cesium is very complex (see Fig. 2). Within the limit of 372 pm Cs1 has a nine-fold, Cs2 and Cs3 have a ten-fold and Cs4 has a twelve-fold coordination. A schematic view of the irregular coordination of the cesium atoms as well as the connection to the eight-membered ring is displayed in Fig. 2(a)–(d). The average Cs–O bond distances are 3.240, 3.282, 3.275 and 3.349 Å of Cs1, Cs2, Cs3 and Cs4, respectively. The bonding distances are listed in Table 3, where O1 and O2 are the bridging atoms in the ring system.

The packing of the eight-membered rings is displayed in Fig. 3. As can be seen the arrangement of the rings leads to approximately rectangular channel-like holes with a diameter of about 600 pm nearly parallel to the crystallographic *a* axis.

TABLE 3. Cesium–oxygen bond lengths in $Cs_4[TiO(C_2O_4)_2]_2 \cdot 3H_2O$

Cs1–O2a	3.390(5)	Cs2–O5a	3.132(5)
Cs1–O6b	3.092(5)	Cs2–O6c	3.153(7)
Cs1–O8	3.250(5)	Cs2–O7	3.193(6)
Cs1–O11b	3.131(5)	Os2–O9a	3.613(5)
Cs1–O13a	3.165(5)	Cs2–O10	2.967(19)
Cs1–O15a	3.384(4)	Cs2–O13c	3.498(5)
Cs1–O17a	3.356(7)	Cs2–O14a	3.172(7)
Cs1–O18a	3.160(9)	Cs2–O14b	3.334(9)
Cs1–O19a	3.229(9)	Cs2–O18	3.210(6)
⟨Cs1–O⟩	3.240	Cs2–O20	3.724(14)
		⟨Cs2–O⟩	3.282
Cs3–O4a	3.178(4)	Cs4–O1	3.424(7)
Cs3–O5b	3.162(7)	Cs4–O2a	3.581(5)
Cs3–O6a	3.369(5)	Cs4–O3a	3.165(4)
Cs3–O9b	3.307(9)	Cs4–O5b	3.327(5)
Cs3–O10a	2.928(10)	Cs4–O8	3.182(5)
Cs3–O11a	3.347(5)	Cs4–O9b	3.611(12)
Cs3–O13b	3.229(8)	Cs4–O12	3.222(5)
Cs3–O17b	3.045(6)	Cs4–O15a	3.195(4)
Cs3–O20a	3.630(12)	Cs4–O19a	3.458(10)
Cs3–O21b	3.554(14)	Cs4–O19b	3.334(9)
⟨Cs3–O⟩	3.275	Cs4–O21b	3.178(18)
		Cs4–O21a	3.526(13)
		⟨Cs4–O⟩	3.349

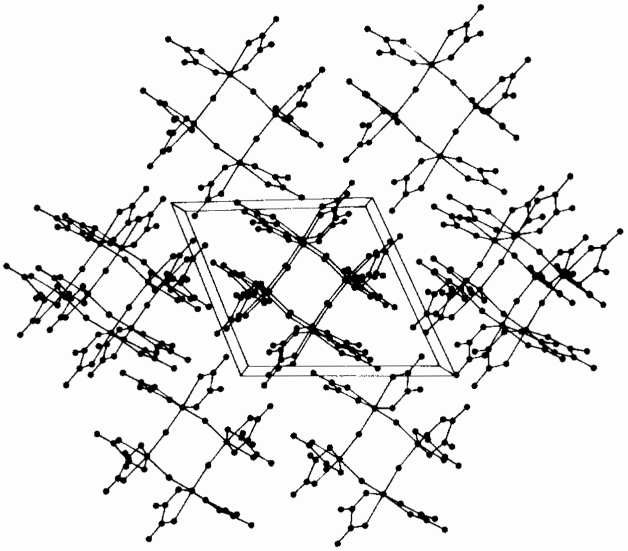

Fig. 3. View along the crystallographic *a* axis in $Cs_4[TiO(C_2O_4)_2]_2 \cdot 3H_2O$.

In the following discussion we distinguish oxygen atoms which have bonds to titanium and carbon atoms (bridging oxygen atoms), oxygen atoms which are bonded to titanium only (ring oxygen atoms) and oxygen atoms which have a bond to carbon only (terminal oxygen atoms). The Cs1 atom (Fig. 2(a)) is connected to one ring oxygen atom (O2) and to three bridging oxygen atoms of the same ring system. The coordination sphere is completed by one water oxygen atom (O19) and four terminal oxygen atoms of oxalato groups of a neighbouring ring system. In contrast, the Cs2 atom has only one bond to a bridging oxygen atom (O7) and eight bonds to terminal oxygen atoms of two different ring systems. The ten-fold coordination is completed by one water oxygen atom (O20) (cf. Fig. 2(b)). The Cs3 atom has only bonds to terminal oxygen atoms and two water oxygen atoms (O20, O21). The Cs4 atom is located above the eight-membered ring. It exhibits bonds to two ring oxygen atoms and to four bridging oxygen atoms of the same ring system. Furthermore, Cs4 shows bonds to three water oxygen atoms and to two terminal oxygen atoms of a different ring system.

TABLE 4. Connection scheme of the O–Cs–O bonds[a]

Cs1	Cs3	Cs4
O8(b)		O8(b)
O2a(r)		O2a(r)
O15a(t)		O15a(t)
O19a(w)		O19a(w)
	O5b(t)	O5b(t)
	O9b(t)	O9b(t)
	O17b(t)	O17b(t)
	O21b(w)	O21b(w)

[a] b = bridging, r = ring, t = terminal, w = water.

TABLE 5. Bond lengths and angles in the four oxalato groups of $Cs_4[TiO(C_2O_4)_2]_2 \cdot 3H_2O$

	C_A–O_A	C_A–O_C	C_B–O_B	C_B–O_D
1	1.288(7)	1.229(8)	1.284(9)	1.218(7)
2	1.277(7)	1.212(7)	1.275(7)	1.220(9)
3	1.279(9)	1.220(7)	1.281(8)	1.219(9)
4	1.312(7)	1.218(8)	1.281(8)	1.221(8)
	Ti–O_A	Ti–O_B	C_A–C_B	
1	1.988(6)	1.993(6)	1.539(10)	
2	2.087(4)	2.087(4)	1.527(12)	
3	2.044(5)	2.095(4)	1.543(11)	
4	2.018(6)	2.018(6)	1.536(10)	
	O_C–C_A–O_A	O_C–C_A–C_B	O_A–C_A–C_B	
1	124.3(1)	122.2(1)	113.4(1)	
2	124.5(1)	121.8(1)	113.8(1)	
3	126.2(1)	121.1(2)	112.9(1)	
4	124.5(1)	123.2(1)	112.5(1)	
	O_B–C_B–O_D	O_D–C_B–C_A	O_B–C_B–C_A	
1	126.3(1)	120.9(1)	112.8(1)	
2	125.8(1)	121.8(1)	112.9(1)	
3	125.5(2)	121.2(1)	113.5(1)	
4	125.8(1)	123.1(2)	113.6(1)	

TABLE 6. Deviations from planarity in the five-membered rings (in Å)

Plane I		Plane II		Plane III		Plane IV	
Ti1	−0.0311	Ti1	−0.0346	Ti2	−0.0375	Ti2	0.0331
O3	0.0328	O7	0.0429	O11	0.0542	O15	−0.0608
O4	0.0402	O8	0.0385	O12	0.0348	O16	−0.0633
C1	−0.0134	C3	−0.0278	C5	−0.0431	C7	0.0314
C2	−0.0285	C4	−0.0190	C6	−0.0084	C8	0.0396
PI–PII 92.2°				PII–PIII 89.6°			
PI–PIII 5.1°				PII–PIV 21.5°			
PI–PIV 93.2°				PIII–PIV 89.2°			

In summary, the eight-membered ring systems are held together by O–Cs–O bonds leading to a complex connecting scheme. In Table 4 this scheme is summarized in a formal way. The Cs1 and Cs4 atoms have bonds to four common oxygen atoms; Cs3 and Cs4, on the other hand, are connected by four different oxygen atoms.

The bond distances and angles in the four different oxalate groups are listed in Table 5. According to the rows 1–4, C_A represents C1, C3, C5 and C7; C_B represents C2, C4, C6 and C8; O_A and O_B are the bridging oxygen atoms; O_C and O_D are terminal oxygen atoms. The bond lengths between the carbon atoms and the terminal oxygen atoms are typical for (C=O) double bonds. The bond distances between carbon and the bridging oxygen atoms are significantly larger indicative of a weakening of the (C=O) double bond. Two oxygen, two carbon atoms and one titanium atom build a five-membered ring. The deviations of planarity of these different rings as well as the angles between the rings are listed in Table 6.

Supplementary material

Tables of calculated and observed structure factors as well as of the anisotropic temperature factors are available from the authors on request.

References

1 J. A. Ibers, *Nature (London), 197* (1963) 686.

2 G. D. Smith, C. N. Caughlan and J. A. Campbell, *Inorg. Chem., 11* (1972) 2989.

3 G. Lundgren, *Ark. Kemi, 10* (1956) 397–413.

4 I. Tordjman, R. Masse and J. C. Guitel, *Z. Kristallogr., 139* (1974) 103–115.

5 G. M. H. Van de Velde, S. Harkema and P. J. Gellings, *Inorg. Nucl. Chem. Lett., 9* (1973) 1169–1173.

6 G. M. H. Van de Velde, S. Harkema and P. J. Gellings, *Inorg. Chim. Acta, 11* (1974) 243–252.

7 N. Dwyer, L. Puppe, J. W. Buchler and W. R. Scheidt, *Inorg. Chem., 14* (1975) 1782–1785.

8 G. E. Form, E. S. Raper, R. E. Oughtred and H. M. M. Shearer, *J. Chem. Soc., Chem. Commun., 34* (1972) 945.

9 F. Brisse and M. Haddad, *Inorg. Chim. Acta, 24* (1977) 173–177.

10 *SHELXTL-plus,* Release 4.0, Siemens Analytical X-Ray Instruments Inc., USA, 1990.

11 *International Tables for X-ray Crystallography,* Vol. IV, Kynoch Press, Birmingham, 1974, pp. 99 ff.; R. F. Stewart, E. R. Davidson and W. T. Simpson, *J. Chem. Phys., 42* (1965) 3175.

12 A. Fester, W. Bensch and M. Trömel, *Z. Kristallogr., Suppl. 3* (1991) 71.

13 M. Trömel, *Acta Crystallogr., Sect. B, 39* (1983) 664–669.

14 A. Fester, *Ph.D. Thesis,* Institut für Anorganische Chemie, Frankfurt am Main, 1990.