Parise, J. B. (1985). *J. Chem. Soc. Chem. Commun.* pp. 606–607.
Sheldrick, G. M. (1976). *SHELX76. Program for Crystal Structure Determination.* Univ. of Cambridge, England.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Wilson, S. T., Lok, B. M., Messina, C. A., Cannon, T. R. & Flanigen, E. M. (1982). *J. Am. Chem. Soc.* **104**, 1146–1147.

Acta Cryst. (1994). C**50**, 850–852

Dipotassium Bis(oxalato)oxotitanate(IV) Dihydrate

A. Fester, W. Bensch and M. Trömel

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

(*Received* 9 *November* 1992; *accepted* 23 *June* 1993)

Abstract

The anions of the title compound, $K_2[TiO(C_2O_4)_2].2H_2O$, form eight-membered rings of four Ti and four O atoms. Each Ti atom is in a distorted octahedral environment. Distances between Ti and O in the non-planar ring system, possessing an inversion centre, range from 1.789 (3) to 2.138 (3) Å. The K ions exhibit eight- or tenfold coordination with typical distances between 2.649 (17) and 3.158 (5) Å. Some of the K ions and the water molecules are disordered.

Comment

In contrast to well known ions like VO^{2+} and VO^{3+}, the corresponding titanium(IV) ions with a Ti=O double bond have not been found until now. The only well characterized compound with a rather short (1.619 Å) Ti—O bond is a titanyl porphyrine (Dwyer, Puppe, Buchler & Scheidt, 1975). In contrast to the chain structures found in *e.g.* $TiOSO_4$ (Lundgren, 1956) or $KTiOPO_4$ (Tordjman, Masse & Guitel, 1974), previous investigation of alkali or ammonium titanyl oxalates showed that these compounds exhibit ring systems (Van de Velde, Harkema & Gellings, 1974; Fester, 1990; Fester, Bensch & Trömel, 1991). Potassium bis(oxalato)oxotitanate(IV) hydrate was prepared in order to gain more information about the disorder phenomena found in the lithium and sodium compounds (Fester, Bensch & Trömel, 1991, 1992*a*).

Important bond angles and distances are summarized in Table 2. The atom numbering corresponds to that shown in Fig. 1. Like the other alkali oxoalato titanates, $K_2[TiO(C_2O_4)_2].2H_2O$ shows eight-membered ring systems with Ti—O bond lengths of ~1.80 Å. Fig. 1 shows this ring system and Fig. 2 presents a view of the unit cell (cations and water of crystallization omitted for clarity). Each Ti atom has a distorted octahedral environment; bond angles and distances in the octahedra are given in Table 2 as well as distances and angles for the four different oxalate groups. The bond lengths between the terminal O and C atoms are typical of C=O double bonds.

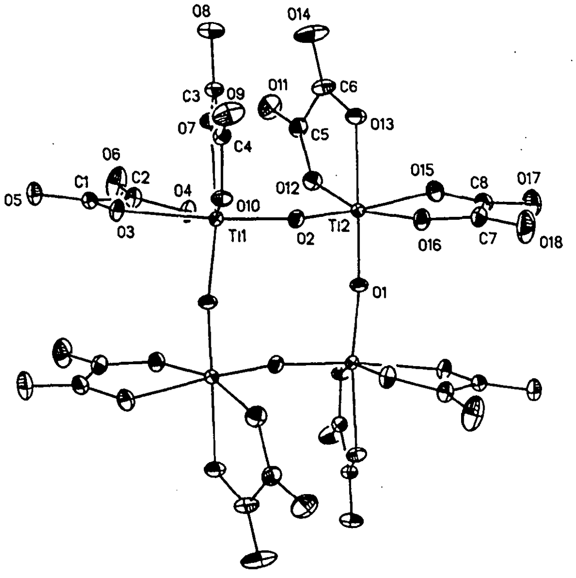

Fig. 1. View of the eight-membered ring system. Elliposids are drawn at the 25% probability level.

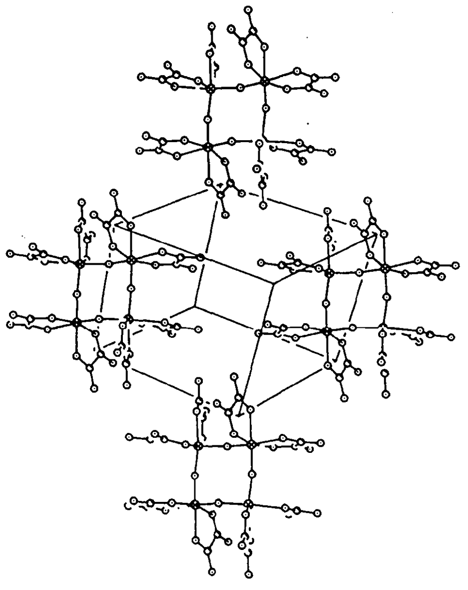

Fig. 2. View of the unit cell, drawn without cations and water of crystallization for clarity.

As can be seen from the displacement parameters in Table 1, some of the water molecules (O19–O28) as well as two of the K ions are disordered. The average K···O distances for K1 to K3 are 2.827 (2), 2.868 (3) and 2.869 (3) Å. The high displacement parameters of K4 and K5 can be explained by their significantly longer average distances [2.884 (3) and 2.887 (4) Å]. This agrees well with the results of structure investigations of the other alkali titanyl oxalates. In the series from the lithium to the caesium compound, a decrease in the disorder of the water of crystallization and the cations is observed. In the lithium compound, the water is only bonded to Li ions. This leads to strong disorder. Only some of the cations could be located (Fester, Bensch & Trömel, 1992*b*). In contrast to these results, caesium titanyl oxalate shows no disorder closely related to the large cations (Fester, Bensch & Trömel, 1992*a*). The potassium compound exhibits an intermediate position. Here the K ions exhibit eight- or tenfold coordination with a rather complex connection scheme. Contacts are observed to O atoms of the ring system as well as the water molecules. The K···O contacts in the range 2.649–3.158 Å have been deposited as part of the supplementary material.

Experimental

A 0.5 *M* solution was prepared by disolving freshly precipitated aqueous TiO_2 in the calculated amount of HCl (Fester, 1990) rather than by hydrolysis of $TiCl_4$ in water. Two equivalents of oxalic acid were added carefully. Four equivalents of KOH were then added slowly under cooling with ice and stirring. This process can take up to several hours to avoid the precipitation of aqueous TiO_2. Half the volume of ethanol was added very carefully to the clear solution during the course of one day in order to obtain two separated layers. $K_2[TiO(C_2O_4)_2].2H_2O$ began to crystallize within several days and was isolated in a yield of 86%. Analysis: found, K 21.9, Ti 13.4, $(C_2O_4)^{2-}$ 49.8, H_2O 9.9%; calculated for $K_2[TiO(C_2O_4)_2].2H_2O$, K 22.0, Ti 13.5, $(C_2O_4)^{2-}$ 49.7, H_2O 10.2%.

Crystal data

$K_2[TiO(C_2O_4)_2].2H_2O$
$M_r = 354.17$
Triclinic
$P\bar{1}$
$a = 9.830$ (2) Å
$b = 11.098$ (2) Å
$c = 11.746$ (2) Å
$\alpha = 68.37$ (3)°
$\beta = 84.90$ (3)°
$\gamma = 76.24$ (3)°
$V = 1156.99$ Å^3
$Z = 4$
$D_x = 2.033$ Mg m^{-3}
$D_m = 2.04$ Mg m^{-3}
Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 25 reflections
$\theta = 10$–30°
$\mu = 1.50$ mm^{-1}
$T = 273$ K
Prism
0.3 × 0.3 × 0.2 mm
Colourless

Data collection

Stoe AEDII diffractometer
ω scans
Absorption correction: none
7112 measured reflections
6748 independent reflections
4469 observed reflections [$I > 3\sigma(I)$]
$R_{\rm int} = 0.0124$
$\theta_{\rm max} = 30°$
$h = -2 \rightarrow 14$
$k = -16 \rightarrow 16$
$l = -16 \rightarrow 16$
3 standard reflections
frequency: 60 min
intensity variation: no decay

Refinement

Refinement on F
$R = 0.0541$
$wR = 0.0796$
$S = 2.6595$
4469 reflections
335 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F) + 0.0004F^2]$
$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 1.12$ e Å^{-3}
$\Delta\rho_{\rm min} = -1.40$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	s.o.f.	x	y	z	$U_{\rm eq}$
Ti1	1	0.0412 (1)	0.3992 (1)	0.2184 (1)	0.020 (1)
Ti2	1	0.1670 (1)	0.3031 (1)	−0.0344 (1)	0.021 (1)
K1	1	−0.4174 (1)	0.1305 (1)	0.5497 (1)	0.033 (1)
K2	0.5	1/2	1/2	1/2	0.035 (1)
K3	1	0.2140 (1)	0.0606 (1)	−0.2934 (1)	0.050 (1)
K4	1	0.1880 (2)	−0.2855 (1)	0.2373 (2)	0.092 (1)
K5†	0.5	0.2769 (6)	0.5952 (6)	0.0045 (5)	0.117 (2)
O1	1	−0.0427 (3)	0.5744 (3)	0.1477 (3)	0.030 (1)
O2	1	0.1310 (4)	0.3736 (3)	0.0870 (3)	0.029 (1)
O3	1	−0.0786 (3)	0.4013 (3)	0.3789 (3)	0.029 (1)
O4	1	−0.1096 (3)	0.3080 (3)	0.2151 (3)	0.030 (1)
O5	1	−0.2579 (4)	0.3273 (4)	0.4916 (3)	0.036 (1)
O6	1	−0.2707 (5)	0.2007 (5)	0.3255 (4)	0.061 (2)
O7	1	0.1444 (3)	0.2129 (3)	0.3371 (3)	0.030 (1)
O8	1	0.3234 (4)	0.1117 (3)	0.4707 (3)	0.042 (1)
O9	1	0.3800 (4)	0.3616 (4)	0.4116 (4)	0.048 (2)
O10	1	0.1918 (3)	0.4437 (3)	0.2894 (3)	0.027 (1)
O11	1	0.0052 (5)	−0.0170 (4)	0.1475 (5)	0.062 (2)
O12	1	0.0400 (4)	0.1781 (3)	0.0183 (3)	0.036 (1)
O13	1	0.2911 (4)	0.1328 (3)	0.0896 (3)	0.036 (1)
O14	1	0.2776 (6)	−0.0664 (4)	0.2316 (5)	0.076 (2)
O15	1	0.2591 (4)	0.2204 (4)	−0.1618 (3)	0.036 (1)
O16	1	0.3368 (3)	0.3812 (3)	−0.0857 (3)	0.033 (1)
O17	1	0.4100 (5)	0.2493 (5)	−0.3167 (4)	0.063 (2)
O18	1	0.5091 (5)	0.4092 (5)	−0.2245 (5)	0.069 (2)
O19	1	0.0510 (5)	0.3232 (4)	−0.3880 (4)	0.049 (2)
O20†	0.7	0.4780 (8)	0.3804 (7)	0.1350 (7)	0.062 (2)
O21†	0.4	0.4521 (14)	−0.1042 (13)	−0.1904 (13)	0.064 (3)
O22†	0.3	0.4857 (14)	−0.0967 (13)	−0.2456 (13)	0.039 (3)
O23†	0.1	0.402 (3)	−0.071 (3)	−0.100 (3)	0.027 (6)
O24†	0.3	−0.0246 (16)	0.0441 (15)	−0.4229 (14)	0.052 (3)
O25†	0.1	0.025 (4)	0.007 (3)	−0.461 (3)	0.031 (7)
O26†	0.3	0.2753 (15)	−0.2916 (14)	−0.0060 (13)	0.048 (3)
O27†	0.5	0.4362 (12)	0.4565 (12)	0.0871 (11)	0.071 (3)
O28†	0.3	0.2553 (18)	−0.1655 (18)	0.0060 (16)	0.065 (4)
C1	1	−0.1777 (4)	0.3390 (4)	0.4036 (4)	0.026 (1)
C2	1	−0.1910 (5)	0.2760 (5)	0.3087 (4)	0.030 (2)
C3	1	0.2500 (5)	0.2099 (4)	0.3957 (4)	0.025 (1)
C4	1	0.2811 (5)	0.3481 (4)	0.3661 (4)	0.026 (1)
C5	1	0.0780 (6)	0.0645 (5)	0.1034 (5)	0.039 (2)
C6	1	0.2290 (6)	0.0378 (5)	0.1467 (5)	0.043 (2)
C7	1	0.4101 (5)	0.3607 (5)	−0.1772 (5)	0.038 (2)
C8	1	0.3582 (6)	0.2686 (5)	−0.2246 (5)	0.038 (2)

† Refined isotropically.

Table 2. *Selected geometric parameters* (Å, °)

Ti1—O1	1.822 (3)	Ti1—O2	1.789 (3)
Ti1—O3	2.138 (3)	Ti1—O4	1.994 (4)
Ti1—O7	2.092 (3)	Ti1—O10	2.001 (4)
Ti2—O1^{i}	1.810 (3)	Ti2—O2	1.836 (4)
Ti2—O12	1.980 (4)	Ti2—O13	2.092 (3)
Ti2—O15	2.068 (4)	Ti2—O16	2.006 (4)
C1—C2	1.548 (8)	C3—C4	1.543 (6)
C5—C6	1.537 (9)	C7—C8	1.528 (9)
C1—O3	1.278 (6)	C3—O7	1.283 (6)
C5—O12	1.281 (5)	C7—O16	1.300 (7)
C1—O5	1.229 (6)	C3—O8	1.232 (5)
C5—O11	1.211 (8)	C7—O18	1.219 (8)
C2—O4	1.290 (6)	C4—O10	1.305 (5)
C6—O13	1.283 (7)	C8—O15	1.266 (7)
C2—O6	1.229 (8)	C4—O9	1.214 (7)
C6—O14	1.239 (6)	C8—O17	1.223 (8)
O1—Ti1—O2	98.9 (1)	O1—Ti1—O10	91.4 (2)
O1—Ti1—O7	165.2 (2)	O1—Ti1—O4	102.8 (2)
O1—Ti1—O3	87.1 (1)	O2—Ti1—O7	92.7 (1)
O2—Ti1—O10	100.0 (2)	O2—Ti1—O3	170.6 (2)
O2—Ti1—O4	94.8 (2)	O3—Ti1—O4	76.7 (2)
O4—Ti1—O7	85.3 (1)	O4—Ti1—O10	157.7 (1)
O3—Ti1—O7	82.7 (1)	O3—Ti1—O10	87.0 (1)
O7—Ti1—O10	77.4 (1)	O2^{i}—Ti2—O1	99.1 (2)
O2—Ti2—O13	88.7 (1)	O2—Ti2—O15	165.6 (2)
O2—Ti2—O12	99.6 (2)	O2—Ti2—O16	90.3 (2)
O1^{i}—Ti2—O16	100.0 (1)	O1^{i}—Ti2—O12	91.9 (2)
O1^{i}—Ti2—O13	167.8 (2)	O1^{i}—Ti2—O15	90.6 (1)
O13—Ti2—O12	77.6 (1)	O13—Ti2—O15	83.5 (1)
O13—Ti2—O16	89.2 (1)	O12—Ti2—O15	90.6 (2)
O12—Ti2—O16	163.2 (1)	O15—Ti2—O16	77.5 (2)
O5—C1—O3	126.3 (5)	O8—C3—O7	127.2 (5)
O11—C5—O12	125.4 (6)	O16—C7—O18	125.5 (7)
O5—C1—C2	120.7 (5)	O8—C3—C4	119.4 (5)
O11—C5—C6	121.8 (4)	O18—C7—C8	121.3 (6)
O3—C1—C2	113.0 (4)	O7—C3—C4	113.4 (3)
O12—C5—C6	112.8 (5)	O16—C7—C8	113.2 (5)
O4—C2—O6	125.1 (6)	O10—C4—O9	125.6 (5)
O13—C6—O14	126.5 (6)	O15—C8—O17	126.1 (7)
O6—C2—C1	121.4 (5)	O9—C4—C3	121.5 (3)
O14—C6—C5	119.7 (6)	O17—C8—C7	120.1 (5)
O4—C2—C1	113.6 (5)	O10—C4—C3	113.0 (4)
O13—C6—C5	113.8 (4)	O15—C8—C7	113.8 (5)

Symmetry code: (i) $-x, 1-y, -z$.

Preliminary Weissenberg photographs were used to check the quality of the chosen crystal and to determine the unit-cell dimensions. The structure was solved by direct methods using the *SHELXTL-Plus* program system (Sheldrick, 1990). All non-H atoms were located by difference synthesis. The refinement of the population parameters of the disordered water molecules was carried out by fixing the temperature factors at a reasonable value. In the final stages, the temperature factors were refined isotropically. Chemical analysis clearly indicates two water molecules in the formula unit. Omitting O23 and O26, both of which have an occupation factor of 0.1, leads to an increase of the R factor from 0.0541 to 0.0578 and ΔF then shows two maxima of 1.59 and 1.48 e Å^{-3} close to O21 and O22. Refinement was by full-matrix least-squares methods. The weighting scheme shows no significant dependence on $(\sin\theta/\lambda)$ and $F_o/F_{o\,\max}$.

Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71743 (32 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: SH1038]

References

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

Fester, A. (1990). PhD thesis, Institut für Anorganische Chemie, Univ. of Frankfurt am Main, Germany.

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

Fester, A., Bensch, W. & Trömel, M. (1992*a*). *Inorg. Chim. Acta*, **193**, 99–103.

Fester, A., Bensch, W. & Trömel, M. (1992*b*). *Inorg. Chim. Acta*, Submitted.

Lundgren, G. (19856). *Ark Kemi*, **10**, 397–413.

Sheldrick, G. M. (1990). *SHELXTL-Plus*. Release 4.0. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

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

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

Acta Cryst. (1994). C**50**, 852–854

Microcrystal Structure Determination of AlPO₄-CHA Using Synchrotron Radiation

MARJORIE M. HARDING AND B. M. KARIUKI

Deparment of Chemistry, University of Liverpool,
PO Box 147, Liverpool L69 3BX, England

(*Received* 26 *November* 1993; *accepted* 7 *January* 1994)

Abstract

Data were recorded from a very small crystal of $AlPO_4$-CHA [trialuminum morpholinium fluoride tris(phosphate), $C_4H_{10}NO^+.Al_3(PO_4)_3F^-$] using synchrotron radiation. The aluminophosphate framework forms a three-dimensional network of channels in which F atoms form bridges between octahedral Al atoms. The N atom of the template (morpholine) is hydrogen bonded to framework O atoms.

Comment

Knowledge of the structure of zeolitic materials is often required in order to rationalize their ion-exchange, molecular sieving and catalytic properties. Synthetic zeolites are frequently available only as polycrystalline powders and so powder diffraction is the common method of structure determination. Data collection using high-intensity radiation sources and very small single crystals has also been shown to be viable, and structures of aluminophosphates and other materials have been obtained (Cheetham, Harding, Haggitt, Mingos & Powell, 1993; Harding, Kariuki, Mathews, Smith & Braunstein, 1994; Cheetham, Harding, Rizkallah, Kaučič & Rajić 1991; Helliwell *et al.*, 1993).

Acta Crystallographica Section C
ISSN 0108-2701 ©1994