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## Hexaaquatitanium(III) Tris(*p*-Toluenesulfonate) Trihydrate

MANUEL A. S. AQUINO, WILLIAM CLEGG,\* QIU-TIAN LIU  
AND A. GEOFFREY SYKES

*Department of Chemistry, University of Newcastle  
upon Tyne, Newcastle upon Tyne NE1 7RU, England*

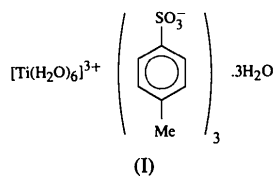
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### Abstract

The crystal structure of [Ti(H<sub>2</sub>O)<sub>6</sub>](*p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>)<sub>3</sub>·3H<sub>2</sub>O consists of discrete cations, anions and solvate water molecules, all linked by a hydrogen-bonding network. Each Ti ion lies on an inversion centre and shows essentially octahedral coordination with Ti—O bonds in the range 2.018 (5)–2.046 (6) Å.

### Comment

There is general interest in completing the structural characterization of the first-row transition metal *M*<sup>III</sup> hexaaqua ions. The V<sup>III</sup>, Cr<sup>III</sup>, Mn<sup>III</sup>, Fe<sup>III</sup> and Co<sup>III</sup> hexaaqua ions, for example, have all been structurally characterized as the alums Cs[M(H<sub>2</sub>O)<sub>6</sub>](SO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (Beattie, Best, Skelton & White, 1981), as has that of Ti<sup>III</sup> (Sygusch, 1974). However, full structural data for only one first-row transition metal ion, V<sup>III</sup> (Cotton, Fair, Lewis, Mott, Ross, Schultz & Williams, 1984), and one second-row transition metal ion, Ru<sup>III</sup> (Bernhard, Bürgi, Hauser, Lehmann & Ludi, 1982), forming [M(H<sub>2</sub>O)<sub>6</sub>]X<sub>3</sub> complexes have been reported. The *p*-toluenesulfonate anion (pts<sup>−</sup>) has proved successful in the past in crystallizing hexaaqua ions such as those of Ru<sup>II</sup> and Ru<sup>III</sup> (Bernhard *et al.*, 1982), Cu<sup>II</sup> (Couldwell, Prout, Robey, Taylor & Rossotti, 1978) and Zn<sup>II</sup> (Hargreaves, 1957). We report here the structure of the *p*-toluenesulfonate salt of [Ti(H<sub>2</sub>O)<sub>6</sub>]<sup>3+</sup>, [Ti(H<sub>2</sub>O)<sub>6</sub>](*p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>)<sub>3</sub>·3H<sub>2</sub>O, (I).



The structure contains discrete [Ti(H<sub>2</sub>O)<sub>6</sub>]<sup>3+</sup> cations, pts<sup>−</sup> anions and solvate water molecules (Fig. 1). Each of the two crystallographically independent Ti ions lies on an inversion centre and is coordinated in an essentially octahedral geometry by six water molecules as ligands. Bond lengths and angles within the cations are unexceptional, with a small range of Ti—O distances [2.018 (5)–2.046 (6) Å], similar to the lengths observed for the caesium titanium alum (Sygusch, 1974). The Ti—O bonds are longer than the V—O bonds in the corresponding cation, where the mean distance is 1.995 Å (Cotton *et al.*, 1984). A decrease in the *M*<sup>III</sup>—O distance such as this is expected on changing the configuration of the central metal ion from *d*<sup>1</sup> to *d*<sup>2</sup> (Cotton & Wilkinson, 1988).

Two-thirds of the coordinated water molecules were refined with similarity restraints on their geometry; the H atoms of the others were not located in difference syntheses. The orientations of these ligands were allowed to refine freely, but in each case the result placed the Ti—O bond essentially in or close to the ligand

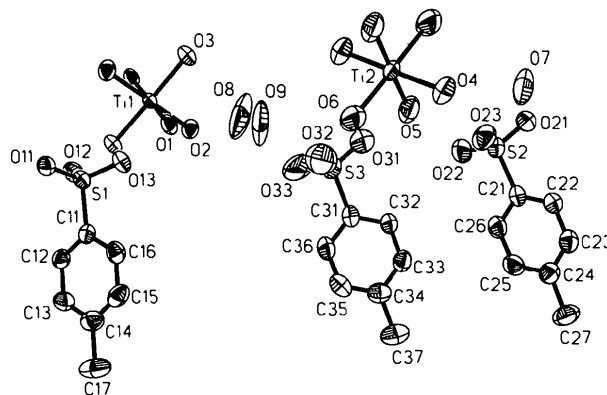


Fig. 1. The atom-labelling scheme for the cations, anions and water molecules, showing 50% probability displacement ellipsoids.

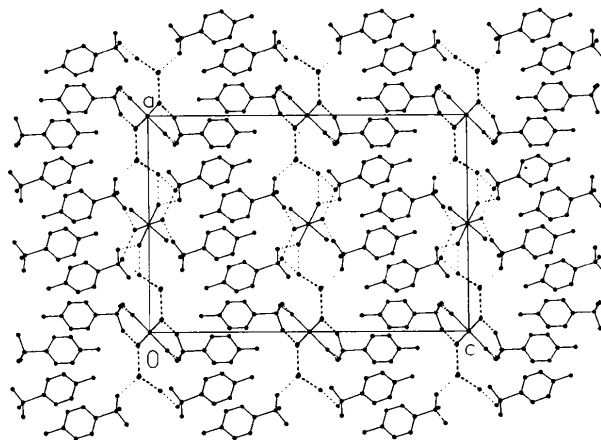


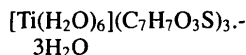
Fig. 2. The packing seen in parallel projection along the *y* axis.

plane, indicating an essentially planar bonding arrangement about the O atoms. All the coordinated and uncoordinated water molecules and most of the O atoms of the  $\text{pts}^-$  anions are involved in hydrogen bonding, with O...O distances in the range 2.53–2.98 Å. The hydrogen bonding forms a two-dimensional sheet network parallel to the  $xy$  plane of the crystal structure with all the O atoms lying within slabs less than 5.4 Å thick centred at  $z = 0$  and  $z = \frac{1}{2}$ . The  $p$ -tolyl substituents of the anions protrude from these slabs, separating them with hydrocarbon regions in which only van der Waals contacts are found. The structure is thus highly layered, with hydrophilic and hydrophobic sections alternating along the  $z$  axis (Fig. 2).

## Experimental

A solution of titanium(III) sulfate (BDH, Technical) in 23%  $w/v$  aqueous sulfuric acid was diluted to about 0.3 M  $\text{H}^+$  and loaded, under nitrogen, on a Dowex cation-exchange column. The column was washed with water and the purple  $\text{Ti}^{\text{III}}$  band eluted with 4 M Hpts. The solution was cooled to 277 K and deposited flat purple needles after about seven days.

### Crystal data



$M_r = 723.61$

Monoclinic

$P2_1/c$

$a = 17.519(2) \text{ \AA}$

$b = 7.1971(8) \text{ \AA}$

$c = 25.835(3) \text{ \AA}$

$\beta = 90.487(11)^\circ$

$V = 3257.3(6) \text{ \AA}^3$

$Z = 4$

$D_x = 1.476 \text{ Mg m}^{-3}$

Mo  $K\alpha$  radiation

$\lambda = 0.71073 \text{ \AA}$

Cell parameters from 32

reflections

$\theta = 10.74\text{--}12.44^\circ$

$\mu = 0.51 \text{ mm}^{-1}$

$T = 240(2) \text{ K}$

Needle

$0.64 \times 0.24 \times 0.16 \text{ mm}$

Purple

### Data collection

Stoe Siemens diffractometer  
 $\omega/\theta$  scans with on-line  
profile fitting (Clegg,  
1981)

Absorption correction:  
empirical

$T_{\min} = 0.634$ ,  $T_{\max} =$   
0.682

5555 measured reflections  
4260 independent reflections

2663 observed reflections  
 $[I > 2\sigma(I)]$

$R_{\text{int}} = 0.0597$

$\theta_{\text{max}} = 22.50^\circ$

$h = -18 \rightarrow 18$

$k = -7 \rightarrow 7$

$l = -26 \rightarrow 27$

3 standard reflections

frequency: 60 min  
intensity decay: none

### Refinement

Refinement on  $F^2$

$R[F^2 > 2\sigma(F^2)] = 0.0656$

$wR(F^2) = 0.2280$

$S = 1.049$

4252 reflections

421 parameters

$w = 1/[\sigma^2(F_o^2) + (0.0994P)^2$   
 $+ 13.4428P]$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} < 0.001$

$\Delta\rho_{\text{max}} = 0.94 \text{ e \AA}^{-3}$

$\Delta\rho_{\text{min}} = -0.51 \text{ e \AA}^{-3}$

Extinction correction: none

Atomic scattering factors

from *International Tables*  
for *Crystallography* (1992,  
Vol. C, Tables 4.2.6.8 and  
6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters ( $\text{\AA}^2$ )*

$$U_{\text{eq}} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_i \cdot a_j$$

	$x$	$y$	$z$	$U_{\text{eq}}$
Ti1	0	0	0	0.0294 (4)
O1	0.0564 (2)	0.2035 (7)	0.0381 (2)	0.0417 (12)
O2	0.0607 (3)	-0.1990 (7)	0.0388 (2)	0.0448 (12)
O3	0.0822 (3)	0.0078 (7)	-0.0546 (2)	0.0402 (11)
Ti2	1/2	1/2	0	0.0469 (5)
O4	0.5930 (3)	0.6280 (10)	0.0315 (2)	0.074 (2)
O5	0.5227 (3)	0.2717 (10)	0.0440 (3)	0.076 (2)
O6	0.4288 (4)	0.6034 (13)	0.0554 (2)	0.106 (3)
O7	0.7322 (3)	0.4942 (13)	0.0320 (3)	0.112 (3)
O8	0.2002 (4)	0.2376 (17)	0.0352 (4)	0.178 (6)
O9	0.2056 (4)	-0.2408 (17)	0.0376 (4)	0.183 (6)
S1	-0.08750 (9)	0.4926 (2)	0.10334 (6)	0.0344 (4)
O11	-0.1321 (2)	0.6522 (6)	0.0849 (2)	0.0409 (12)
O12	-0.1250 (3)	0.3176 (7)	0.0917 (2)	0.0466 (13)
O13	-0.0087 (2)	0.4996 (7)	0.0849 (2)	0.0441 (12)
C11	-0.0825 (3)	0.5082 (9)	0.1713 (2)	0.035 (2)
C12	-0.1431 (4)	0.4455 (10)	0.2005 (3)	0.041 (2)
C13	-0.1403 (4)	0.4662 (11)	0.2543 (3)	0.049 (2)
C14	-0.0784 (5)	0.5434 (11)	0.2794 (3)	0.051 (2)
C15	-0.0187 (4)	0.6066 (11)	0.2493 (3)	0.050 (2)
C16	-0.0201 (4)	0.5910 (10)	0.1958 (3)	0.043 (2)
C17	-0.0754 (6)	0.5658 (13)	0.3369 (3)	0.077 (3)
S2	0.68085 (10)	0.0168 (3)	0.09762 (7)	0.0488 (5)
O21	0.7422 (3)	-0.0484 (8)	0.0656 (2)	0.062 (2)
O22	0.6142 (3)	-0.1026 (10)	0.0978 (2)	0.072 (2)
O23	0.6585 (3)	0.2090 (9)	0.0855 (2)	0.071 (2)
C21	0.7152 (4)	0.0241 (10)	0.1619 (3)	0.041 (2)
C22	0.7840 (4)	-0.0592 (11)	0.1748 (3)	0.050 (2)
C23	0.8085 (4)	-0.0544 (11)	0.2259 (3)	0.054 (2)
C24	0.7665 (4)	0.0297 (11)	0.2647 (3)	0.051 (2)
C25	0.6984 (4)	0.1141 (12)	0.2498 (3)	0.057 (2)
C26	0.6728 (4)	0.1113 (11)	0.1997 (3)	0.051 (2)
C27	0.7921 (6)	0.0322 (14)	0.3202 (3)	0.076 (3)
S3	0.36136 (13)	0.0680 (6)	0.10830 (10)	0.0958 (11)
O31	0.4216 (4)	0.0047 (12)	0.0763 (3)	0.096 (2)
O32	0.3513 (6)	0.2733 (18)	0.0982 (3)	0.159 (5)
O33	0.2905 (5)	-0.0133 (21)	0.1040 (3)	0.201 (7)
C31	0.3914 (4)	0.0544 (12)	0.1733 (3)	0.052 (2)
C32	0.4629 (4)	-0.0146 (11)	0.1866 (3)	0.050 (2)
C33	0.4840 (4)	-0.0268 (11)	0.2373 (3)	0.053 (2)
C34	0.4360 (5)	0.0250 (11)	0.2771 (3)	0.053 (2)
C35	0.3646 (5)	0.0954 (12)	0.2630 (3)	0.057 (2)
C36	0.3418 (4)	0.1106 (12)	0.2124 (3)	0.055 (2)
C37	0.4611 (6)	0.0109 (13)	0.3328 (3)	0.073 (3)

Table 2. *Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ )*

Ti1—O1	2.018 (5)	Ti2—O5	2.035 (6)
Ti1—O3	2.026 (4)	Ti2—O4	2.035 (5)
Ti1—O2	2.042 (5)	Ti2—O6	2.046 (6)
O1—Ti1—O3	88.3 (2)	O5—Ti2—O4	89.5 (3)
O1—Ti1—O2	91.1 (2)	O5—Ti2—O6	91.2 (3)
O3—Ti1—O2	89.5 (2)	O4—Ti2—O6	92.7 (3)

One complete unique set of reflections was measured, together with some Friedel opposites; the index limits given above do not indicate a complete sphere of data. In accordance with indications from difference syntheses, H atoms of the anions were geometrically placed and refined with a riding model, those of the methyl groups showing twofold rotational disorder. H atoms of four of the six independent coordinated water molecules were located in difference syntheses and were successfully refined with similarity restraints on O—H distances and H—O—H angles, orientations remaining free. H atoms of the other coordinated and uncoordinated water molecules were not located.

Data collection: *DIF4* (Stoe & Cie, 1988). Cell refinement: *DIF4*. Data reduction: local programs. Program(s) used to

solve structure: *SHELXTL/PC* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *SHELXL93* and local programs.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: MU1139). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

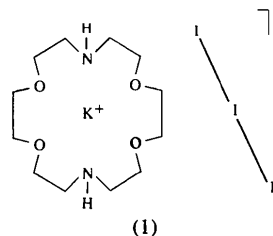
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I<sub>2</sub> to one formula unit of [K(diaza-18-crown-6)]I. The structure can be described as the packing of linear centrosymmetric triiodide anions, I<sub>3</sub><sup>-</sup>, with I—I = 2.9131(8) Å, and centrosymmetric complex cations, [K(diaza-18-crown-6)]<sup>+</sup>.

## Kommentar

Komplexe Kationen sind geeignet, den Einfluß von Form, Größe, und Ladung des Kations auf Polyiodidionen und -verbände zu untersuchen, da sich diese Merkmale durch die Wahl der Zentralatome und Liganden in kleinen Schritten verändern lassen (Tebbe, 1977). Einen besonderen Einfluß auf das Iodgerüst haben koordinativ ungesättigte Komplexe, da diese eine strukturelle Auftrennung in zusätzlich koordinativ gebundene Iodidionen und vernetzende Iodmoleküle erzeugen können (Tebbe & Plewa, 1982). Alkalicryptate erscheinen als große niedriggeladene und weitgehend abgeschirmte Kationen zum Einbau von Polyhalogenidionen in stabilen Festkörpern besonders geeignet, wie wir durch die erstmalige Darstellung eines Dodecaoids [K(2,2,2-Crypt)]<sub>2</sub>I<sub>12</sub> bereits zeigen konnten (Tebbe & Kavoosian, 1993). Man darf nun erwarten, daß insbesondere die großen Alkalimetallionen in Komplexen mit kleineren Kronenethern einen schwachen koordinativen Einfluß auf die Polyiodidverbände behalten. Um diese Vermutung zu überprüfen, haben wir die bisher unbekannte Verbindung [K(2,2-Crypt)]I<sub>3</sub> dargestellt und strukturell untersucht. Der Ligand 2,2-Crypt wird auch als Diaza-18-Krone-6 oder 1,4,10,13-Tetraoxa-7,16-diazacyclooctadecan bezeichnet.



Die salzartige Kristallstruktur enthält das komplexe Kation [K(2,2-Crypt)]<sup>+</sup> und das Triiodid-Anion I<sub>3</sub><sup>-</sup> jeweils auf Lagen der Symmetrie *i*. Der Ligand und das komplexe Kation zeigen im Vergleich mit anderen strukturell untersuchten Verbindungen wie 2,2-Crypt (Herceg & Weiss, 1972), 2,2-Crypt.4CH<sub>4</sub>N<sub>2</sub>S (Weber, 1982), 2,2-Crypt.C<sub>10</sub>H<sub>8</sub>O<sub>2</sub> (Watson, Nagl & Kashyap, 1991) und [K(2,2-Crypt)].SCN (Moras, Metz, Herceg & Weiss, 1972) keine Besonderheiten. Die hier vorliegenden mittleren geometrischen Größen  $d(\text{N—C}) = 1,413(7)$ ,  $d(\text{C—C}) = 1,481(9)$  und  $d(\text{C—O}) = 1,432(8)$  Å,  $\varphi(\text{C—N—C}) = 113,8(5)$ ,  $\varphi(\text{C—C—N}) = 109,7(5)$ ,  $\varphi(\text{C—O—C}) = 113,0(6)$  und  $\varphi(\text{O—C—C}) = 110,5(5)^\circ$ ,  $\tau(\text{C—C—O—C}) = -177,1(6)$ ,  $\tau(\text{O—C—C—O}) = 65,0(6)$ ,  $\tau(\text{N—C—C—O}) = -64,8(6)$

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## Kalium-2,2-Crypt-triiodid†

KARL-FRIEDRICH TEBBE UND ARISTA KAVOOSIAN

*Institut für Anorganische Chemie, Universität zu Köln, Greinstraße 6, D-50939 Köln, Deutschland*

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### Abstract

The title compound, (1,4,10,13-tetraoxa-7,16-diazacyclooctadecane)potassium triiodide, [K(C<sub>12</sub>H<sub>26</sub>N<sub>2</sub>O<sub>4</sub>)]I<sub>3</sub>, has been prepared in ethanol in the presence of dichloromethane by the addition of one molecule of

† Untersuchungen an Polyhalogeniden. 14. Teil 13: Tebbe & Nafepour (1994).