The Structure of μ-Oxalatobis(oxalato)hexaquodititanium(III) Tetrahydrate: A Pentagonal-bipyramidal Titanium Complex

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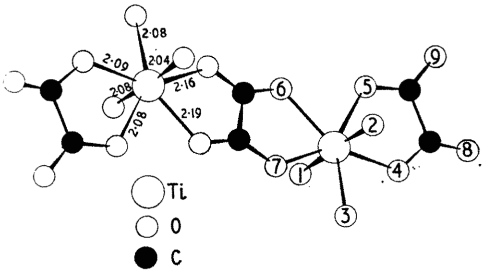
Summary The titanium is in a seven-co-ordinate (pentagonal bipyramid) environment.

FROM spectroscopic evidence $Ti_2\,ox_3,10H_2O$ (ox = oxalate) was assigned[1] a polymeric, six-co-ordinate (octahedral) structure, but a single *X*-ray study now shows the titanium atoms to be seven-co-ordinate(pentagonal bipyramid).

Brown, prismatic crystals of $Ti_2\,ox_3,10H_2O$ ($M = 540{\cdot}0$) are triclinic, spacegroup $P\bar{1}$ with $a = 8{\cdot}242(4)$, $b = 7{\cdot}161(4)$, $c = 9{\cdot}934(4)$ Å, $\alpha = 95{\cdot}30(8)^\circ$, $\beta = 122{\cdot}54(5)^\circ$, $\gamma = 102{\cdot}60(8)^\circ$, $U = 466{\cdot}5$ Å^3, $D_m = 1{\cdot}92(2)$ g.cm.$^{-3}$, $Z = 1$, $D_c = 1{\cdot}922$ g.cm.$^{-3}$. The intensities of 2573 independent reflections ($2\theta \leqslant 60^\circ$) were recorded, using zirconium filtered Mo-K_α radiation, on a GE XRD-5 manual diffractometer by the stationary crystal–stationary counter method. The structure was solved by the Patterson and Fourier methods and 2294 non-zero reflections used to refine the atoms (other than H), which were allowed anisotropic temperature factors, by full-matrix least-squares to the present conventional *R* factor of 0·10.

The molecule possesses a centre of symmetry midway between the carbon atoms of the bridging oxalato group. The configuration about the titanium atoms is approximately pentagonal bipyramidal (see diagram), the two axial and one of the equatorial positions being filled by water molecules. The remaining four equatorial positions are taken up by bridging and chelating oxalato-groups. The four non-bonded water molecules are not shown.



The bond distances Ti–O(oxalate), with standard deviations 0·01 Å, show significant differences; the Ti–O bridging oxalate being longer than the Ti–O terminal oxalate distances. The bond angles between the axial and equatorial positions show considerable distortion from 90° (*cf.* Table), although the angles between atoms in the equatorial plane are all within 2° of the expected 72° for a regular pentagonal-bipyramidal configuration.

Angles between the axial and equatorial positions

O(1)–Ti–O(3)	91·9(2)°	O(2)–Ti–O(3)	84·6(2)°
O(1)–Ti–O(4)	85·0(2)°	O(2)–Ti–O(4)	98·5(2)°
O(1)–Ti–O(5)	99·8(2)°	O(2)–Ti–O(5)	85·9(2)°
O(1)–Ti–O(6)	85·9(2)°	O(2)–Ti–O(6)	94·2(2)°
O(1)–Ti–O(7)	90·3(2)°	O(2)–Ti–O(7)	84·2(2)°

Least-squares plane calculations show that although the equatorial plane defined by atoms Ti, O(3), O(4), O(5), O(6), and O(7) lies at 88° to the bonds O(1)–Ti and O(2)–Ti, the atoms O(5) and O(6) lie at 0·23 Å and 0·27 Å respectively on either side of this plane. It also appears that the bridging oxalato group is planar to within experimental error whereas the terminal oxalato group, contrary to previous observations on Cr ox$_3^{3-}$,[2] K$_2${[MoO$_2$ ox H$_2$O]$_2$O}[3] and Na$_4$Zr ox$_4$,3H$_2$O,[4] is distorted, for although atoms O(8)–C–C–O(4) are planar to within two standard deviations, atoms Ti, O(9) lie 0·11 Å above and atom O(5) 0·16 Å below the plane defined by the titanium atom and the terminal oxalato-group.

Because of the unexpected stereochemistry we have reinvestigated the diffuse reflectance spectrum in the visible region and found bands attributable to *d–d* transitions at 12,300 and 9,400 cm.$^{-1}$. The site symmetry of the titanium atom is approximately D_{5h}, which leads us to assign the observed transitions to $E_2' \rightarrow E_1''$ and $A_1' \rightarrow E_1''$ both of which are symmetry forbidden.

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