Inorganica Chimica Acta, 174 (1990) 205–208

A Tris(oxalato) Titanium(III) Complex: the Preparation and Structure of Potassium Aquatrioxalatotitanate(III) Tetrahydrate

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(Received February 2, 1990)

Abstract

Potassium aquatrioxalatotitanate(III) tetrahydrate has been prepared by the addition of excess potassium oxalate to an aqueous solution of hexaureatitanium(III) chloride. The crystal and molecular structure has been determined by single-crystal, X-ray diffractometry (Mo Kα radiation, 0.7107 Å) and found to be orthorhombic, with unit cell dimensions: $a = 20.746(3)$, $b = 11.532(2)$, $c = 7.328(2)$ Å, space group $Pnma$ and $Z = 4$. The anionic complex consists of a distorted pentagonal-bipyramidal arrangement of seven oxygen atoms around the titanium atom. One axial oxygen atom is provided by the coordinated water molecule and the rest by chelating oxalate ions of which two are in the equatorial plane. Observed bands in the diffuse reflectance spectrum at 9600 and 12 200 cm^{-1}, attributed to d–d electronic transitions, are discussed in relation to the structure.

Introduction

Bis(oxalato) complexes of titanium(III) have been known for a long time [1] and their structures have been investigated and reported [2–4]. Tris(oxalato) complexes are known for other trivalent transition metal ions, but no such complex for titanium(III) has been reported previously. It has now been found that a tris(oxalato) complex is formed when excess potassium oxalate is added to a solution of hexaureatitanium(III) chloride. Elemental analysis of the crystalline product shows that the stoichiometric composition is $K_3Ti(C_2O_4)_3\cdot 5H_2O$. The infrared spectrum is typical of an oxalato complex and shows that the oxalate ligands are non-bridging [5].

The diffuse reflectance spectrum in the visible and near infrared suggests a seven-coordinate (D_{5h}) structure for the complex titanate ion similar to that in $Cs[Ti(ox)_2(H_2O)_3]\cdot 2H_2O$ [3]. A structure, which is approximately pentagonal-bipyramidal, has been confirmed by single-crystal X-ray diffraction measurements.

Experimental

Preparation of $K_3[Ti(ox)_3(H_2O)]\cdot 4H_2O$

The preparation was carried out under nitrogen using aqueous solutions which had been deoxygenated by flushing with nitrogen. A solution of 1.60 g of urea (2.6×10^{-2} mol) in 12 ml of water was heated to 60 °C and 0.80 g of solid $TiCl_3\cdot 6H_2O$ (3.0×10^{-3} mol) added with stirring. To the solution of $[Ti(urea)_6]Cl_3$ produced in this way 2.80 g of potassium oxalate hydrate ($K_2C_2O_4\cdot H_2O$, 1.5×10^{-2} mol) dissolved in 8 ml of hot water was then added dropwise. The mixture was stirred for an hour and then allowed to cool. The dark-red crystalline product was separated from the solution after two days and stored under nitrogen.

Elemental Analysis

Found: K, 22.0; Ti, 9.26; C, 14.1; H, 1.65. Calc. for $K_3Ti(C_2O_4)_3\cdot 5H_2O$: K, 22.6; Ti, 9.22; C, 13.9; H, 1.94%.

Magnetic Susceptibility

Magnetic susceptibility was determined at room temperature (24 °C) using a Faraday balance; $\mu_{eff} = 1.66$ BM.

Infrared Spectrum

The infrared spectrum was recorded by the KBr disc technique using a Perkin-Elmer IR180 spectrophotometer. Absorption bands are observed at 1650(s), 1410(m), 1300(m), 900(w) and 800(m) cm^{-1}.

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0020-1693/90/$3.50

Diffuse Reflectance Spectrum

The diffuse reflectance spectrum of the solid complex was recorded in the range 400 to 2000 nm (25 000 to 5000 cm^{-1}) using a Beckman 5240 spectrophotometer. Two overlapping, low-intensity bands attributable to d–d electron transitions were observed at 9600 and 12 200 cm^{-1}.

X-ray Diffraction

A few single crystals were selected, coated in glue because of instability in air, and photographed (Cu Kα radiation, λ = 1.5418 Å), using oscillation and Weissenberg methods, which gave approximate cell dimensions and established the space group as either $Pna2_1$ (No. 33) or *Pnma* (No. 62). One of the crystals was then irradiated on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.7107 Å). Accurate cell parameters were determined by a least-squares analysis of the setting angles of 24 reflections ($16 \leqslant \theta \leqslant 17°$). During the data collection, the intensities of three reference reflections were monitored every hour and orientation was checked periodically. The data were Lp-processed but no absorption correction applied. Further experimental details of the crystal and data collection are reported in Table 1.

Solution and Refinement of the Structure

The positions of the Ti and K were determined by Direct Methods using SHELXS-86 [6] in the space group *Pnma* and successful refinement of the structure has vindicated this choice. The structure was refined using SHELX-76 [7]; all non-hydrogen atoms were treated anisotropically; no hydrogens were included in the final model; a weighting scheme was applied. Complex neutral atom scattering factors for Ti, K, C and O were taken from Cromer and Mann [8]; dispersion corrections were obtained from Cromer and Liberman [9]. Molecular parameters were calculated using PARST [10] and drawings obtained using PLUTO [11]. All computations were carried out on a VAX computer. Further details of the structure solution and final refinement are shown in Table 1.

TABLE 1. Experimental details of crystal, data collection, structure solution and refinement of $K_3[Ti(oxalate)_3H_2O] \cdot 4H_2O$

Molecular formula	$C_6H_{10}O_{17}K_3Ti$
M_r (g mol^{-1})	519.34
Space group	*Pnma*
a (Å)	20.746(3)
b (Å)	11.532(2)
c (Å)	7.328(2)
V ($Å^3$)	1753.3(7)
Z	4
ρ_c	1.97
$F(000)$(e)	1044
μ(Mo Kα) (cm^{-1})	12.8
Dimensions of crystal (mm)	0.28 × 0.34 × 0.47
Scan mode	$\omega-2\theta$
Scan width in ω (°)	$(0.85 + 0.35 \tan \theta)$
Aperture width (mm)	$(1.12 + 1.05 \tan \theta)$
Scan speed	variable, 40 s max. time
Crystal decay (%)	0.2
No. reflections collected	1532
No. reflections with $I_{rel} > 2\sigma_{Irel}$, N	1399
No. parameters, NP	139
$R = \Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|$	0.045
$R_w = \Sigma w^{1/2}\|\|F_o\| - \|F_c\|\|/\Sigma w^{1/2}\|F_o\|$	0.046
w	$(\sigma^2 F)^{-1}$
$S = (\Sigma\|\|F_o\| - \|F_c\|\|^2/N - NP)^{1/2}$	3.89
Max./min. residual e density ($Å^{-3}$)	0.59/−0.46

Description of the Structure

Final fractional atomic coordinates are reported in Table 2. Figure 1 shows the anion with atomic numbering (atoms for which the numbers are distinguished by primes are symmetry generated).

The Ti, K, one bidentate oxalate and the coordinated water lie on special positions (Wykoff site c, having site-occupancy 0.5). An additional bidentate oxalate and two uncoordinated water molecules of crystallization are on general positions; this model yields the expected stoichiometry $K_3[Ti(oxalate)_3(H_2O)] \cdot 4H_2O$. The complete structure is shown in projection down the b axis (Fig. 2). In the discrete anion, which has crystallographically im-

TABLE 2. Fractional atomic coordinates (×10^4) and temperature factors (U_{eq}) ($Å^2$ × 10^3) with e.s.d.s in parentheses for $K_3[Ti(ox)_3H_2O] \cdot 4H_2O$

Atom	x/a	y/b	z/c	U_{eq}[b]
Ti(1)[a]	942(0)	2500	2006(1)	28(1)
O(1)	131(1)	1432(3)	2436(5)	38(1)
O(2)	1253(1)	773(3)	1569(5)	50(1)
O(11)	−237(2)	−392(3)	2710(6)	61(1)
O(21)	992(2)	−1115(3)	1664(5)	50(1)
C(1)	191(2)	332(4)	2368(7)	39(2)
C(2)	868(2)	−86(4)	1824(6)	40(2)
O(3)[a]	1959(2)	2500	2306(6)	35(1)
O(4)[a]	1056(2)	2500	4795(6)	40(2)
O(31)[a]	2718(2)	2500	4438(8)	97(3)
O(41)[a]	1769(2)	2500	7005(7)	93(3)
C(3)[a]	2156(3)	2500	3924(10)	44(3)
C(4)[a]	1625(3)	2500	5408(9)	48(3)
O(5)[a]	794(2)	2500	−805(6)	52(2)
K(1)[a]	3967(1)	2500	3719(2)	38(1)
K(2)[a]	4767(1)	2500	9061(2)	43(1)
K(3)[a]	2962(1)	2500	8356(3)	63(1)
O(111)	8720(2)	4073(3)	4041(6)	64(2)
O(112)	7536(2)	5327(4)	10039(8)	89(2)

[a] Atom at site occupancy 0.5. [b] $U_{eq} = \frac{1}{3}$(trace of the orthogonalized U_{ij} matrix).

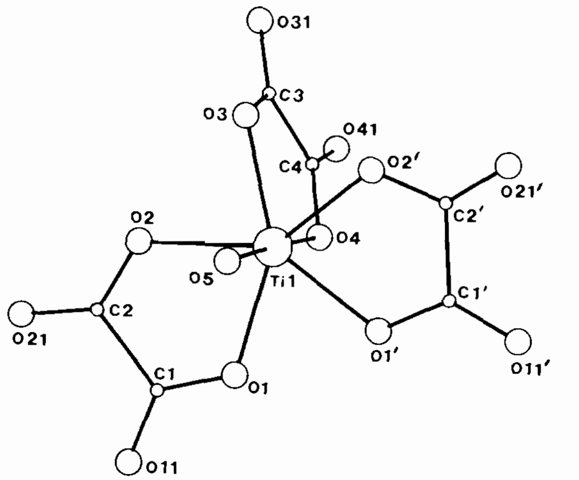

Fig. 1. Atomic numbering for the anion $[Ti(ox)_3(H_2O)]^{3-}$.

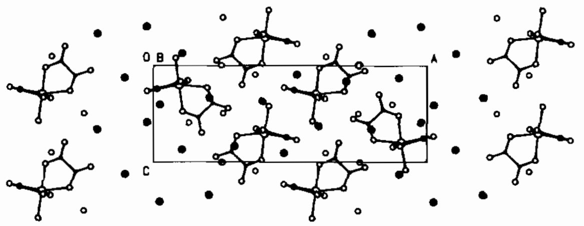

Fig. 2. Projection of the structure down *b*. Open circles: large, Ti; small, O. Closed circles: large, K; small, C.

posed *Cs* (mirror) symmetry, the Ti is seven-coordinate, with the coordinated oxygens describing a pentagonal bipyramid. The axial positions are occupied by the coordinated water (Ti(1)–O(5), 2.083(5) Å) and O(4) of the oxalate (Ti(1)–O(4), 2.057(4) Å). The equatorial positions are occupied by oxalate oxygens O(1), O(2), O(3), O(1)′, O(2)′ (x, $-y + \frac{1}{2}$, z) which have Ti(1)–O in the range 2.109(3)–2.122(4) Å. The bonds to the axial atoms are just shorter than those to the equatorial atoms which difference has been previously observed [3].

The angles subtended at the metal by the two unique oxalates are 73.5(1) and 77.4(2)° for O1,O2 and O3,O4, respectively (see Table 3). There is considerable distortion from D_{5h} symmetry of a regular pentagonal bipyramid, as one oxalate coordinates across both an equatorial (O3) and axial (O4) site yielding O_{ax}–Ti–O_{eq} 77.4(2) and 104.4(2)°, respectively. However, the remaining O_{ax}–Ti–O_{eq} angles are in the range 84.0(1)–96.6(1)°, somewhat closer to 90°.

As is usual for non-bridging oxalate, the bonds from C to the non-coordinated O atoms are significantly shorter than the others (1.207(8)–1.245(5) Å versus 1.254(8)–1.286(6) Å, respectively. One oxalate (C3, C4) is planar as required by the *Cs* symmetry. The remaining oxalate is slightly buckled, with the maximum deviation of a contributing atom from the C_2O_4 plane of 0.02 Å.

Close contacts between O atoms of the structure are reported in Table 4, as are the shortest K···O distances.

TABLE 3. Bond lenghts (Å) and angles (°) for the anion $[Ti(C_2O_4)_3H_2O]^{3-}$ with e.s.d.s in parentheses

Ti(1)–O(1)[a]	2.109(3)	C(1)–O(1)	1.276(6)	C(2)–O(21)	1.220(6)
Ti(1)–O(2)[a]	2.118(3)	C(2)–O(2)	1.286(6)	C(3)–O(31)	1.225(8)
Ti(1)–O(3)	2.122(4)	C(3)–O(3)	1.254(8)	C(4)–O(41)	1.207(8)
Ti(1)–O(4)	2.057(4)	C(4)–O(4)	1.263(7)	C(1)–C(2)	1.539(6)
Ti(1)–O(5)	2.083(5)	C(1)–O(11)	1.245(5)	C(3)–C(4)	1.549(9)
O(1)–Ti(1)–O(2)	73.5(1)	Ti(1)–O(1)–C(1)	119.8(2)		
O(1)–Ti(1)–O(3)	141.1(1)	Ti(1)–O(2)–C(2)	120.9(3)		
O(1)–Ti(1)–O(1)[b]	71.5(2)	Ti(1)–O(3)–C(3)	115.0(4)		
O(2)–Ti(1)–O(2)[b]	140.2(2)	Ti(1)–O(4)–C(4)	117.4(4)		
O(2)–Ti(1)–O(3)	73.3(1)	O(1)–C(1)–O(11)	126.1(4)		
O(1)[b]–Ti(1)–O(2)	144.6(1)	O(11)–C(1)–C(2)	119.6(4)		
O(4)–Ti(1)–O(1)	86.8(1)	O(1)–C(1)–C(2)	114.3(4)		
O(4)–Ti(1)–O(2)	96.6(1)	O(21)–C(2)–C(1)	121.5(4)		
O(4)–Ti(1)–O(3)	77.4(2)	O(2)–C(2)–C(1)	111.3(4)		
O(5)–Ti(1)–O(1)	91.7(1)	O(2)–C(2)–O(21)	127.2(4)		
O(5)–Ti(1)–O(2)	84.0(1)	O(3)–C(3)–O(31)	126.9(7)		
O(5)–Ti(1)–O(3)	104.4(2)	O(31)–C(3)–C(4)	117.5(6)		
O(4)–Ti(1)–O(5)	178.2(2)	O(3)–C(3)–C(4)	115.6(6)		
		O(41)–C(4)–C(3)	120.3(6)		
		O(4)–C(4)–C(3)	114.5(6)		
		O(4)–C(4)–O(41)	125.2(6)		

[a] x, y, z and $x, -y + \frac{1}{2}, z$. [b] $x, -y + \frac{1}{2}, z$.

TABLE 4. Intermolecular contacts (Å) with e.s.d.s in parentheses

O···O contacts indicative of hydrogen bonding possibilities		
O(5)···O(2)	2.811(5)	
O(5)···O(41)	2.582(6)	$x, y, z - 1$
O(111)···O(11)	2.819(6)	$x + 1, -y + \frac{1}{2}, z$
O(111)···O(112)	2.793(6)	$-x + \frac{3}{2}, -y + 1, z - \frac{1}{2}$
O(112)···O(2)	2.822(5)	$-x + 1, y + \frac{1}{2}, -z + 1$
K coordination		
K(1)···O(31)	2.644(5)	
K(1)···O(1)	2.840(3)	$x + \frac{1}{2}, y, -z + \frac{1}{2}$
K(1)···O(21)	2.686(4)	$-x + \frac{1}{2}, -y, z + \frac{1}{2}$
K(1)···O(111)	2.765(4)	$x - \frac{1}{2}, y, -z + \frac{1}{2}$
K(2)···O(1)	2.946(4)	$x + \frac{1}{2}, -y + \frac{1}{2}, -z + \frac{3}{2}$
K(2)···O(11)	2.800(4)	$-x + \frac{1}{2}, -y, z + \frac{1}{2}$
K(2)···O(21)	2.849(4)	$-x + \frac{1}{2}, -y, z + \frac{1}{2}$
K(2)···O(4)	2.803(5)	$x + \frac{1}{2}, -y + \frac{1}{2}, -z + \frac{3}{2}$
K(3)···O(31)	2.915(6)	
K(3)···O(41)	2.666(5)	
K(3)···O(21)	2.966(4)	$-x + \frac{1}{2}, -y, z + \frac{1}{2}$
K(3)···O(111)	3.066(4)	$x - \frac{1}{2}, -y + \frac{1}{2}, -z + \frac{3}{2}$

Discussion

The structure found suggests that the oxalate ligand, with its relatively narrow bite, is more readily accommodated in the pentagonal plane than in axial-to-equatorial chelation. For the two oxalate groups in the equatorial plane bond lengths and angles are close to those found in Cs $[Ti(ox)_2(H_2O)_3]\cdot 2H_2O$ [3] and the non-bridging oxalate in $[Ti_2(ox)_3(H_2O)_6]\cdot 4H_2O$ [2]. Axial to equatorial chelation apparently induces changes in TiO bond lengths (2.06 and 2.12 Å compared with 2.11 and 2.12 Å) and the O–Ti–O bond angle (77.4° compared with 73.5°), giving a structure closely resembling that reported for *trans*-$K_2[Cu(ox)_2(H_2O)_2]$ [12], although it differs considerably from that found in *trans*-diaquadioxalatochromate(III) [13], in which the O–Cr–O angle of 83° is closer to the ideal of 90° for regular six coordination. The angle of 77° causes more deviation from true D_{5h} symmetry than is found in the other bis oxalato complexes of Ti(III).

The absorption bands in the electronic (diffuse reflectance) spectrum at 9600 and 12 200 cm^{-1} are attributed to $E_2' \leftarrow E_1''$ and $A_1' \leftarrow E_1''$ transitions and can be compared with the corresponding bands at 10 500 and 12 500 cm^{-1} in $Cs[Ti(ox)_2(H_2O)_3]\cdot 2H_2O$. The lower frequencies observed can be attributed to the departure from true D_{5h} symmetry in which the Ti–O(3) bond is at an angle to the equatorial plane (16.5° to the TiO(1)O(1)′ plane). This could be expected to decrease the energy of the E_2' term and increase the energy of the E_1'' term.

The room temperature magnetic moment which is just below the spin only value, is consistent with the E_1 ground state and d^1 configuration.

Supplementary Material

A copy of the table of structure factors is available from the authors on request.

Acknowledgements

Margaret L. Niven thanks the University of Cape Town and the FRD for financial assistance and D. J. Eve is grateful to Rhodes University Council for research funding.

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