Isolation and Characterization of Anionic Titanium Tris(glycolate) Complexes

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Introduction

Titanium dioxide is generally considered to be "unreactive" and not a particularly suitable starting material for further titanium chemistry.[1] Nevertheless, preparative titanium chemistry starts with the conversion of raw materials containing titanium oxides by either digestion with concentrated sulfuric acid, the so-called sulfate route, or reaction with coke and chlorine at elevated temperatures to give titanium tetrachloride in the chloride route. It would be advantageous to have other routes available to yield soluble titanium compounds. In recent papers by Laine and co-workers[2−4] and by our group,[5] it was demonstrated that silica (SiO_2) can be dissolved in glycol (1,2-ethanediol) in the presence of a base to give penta- and hexacoordinate complexes.

Here we report the successful synthesis and structural characterization of soluble titanium glycolato complexes obtained from the reaction of titanium dioxide or titanium isopropoxide with glycol in the presence of alkali metal hydroxides.

Experimental Section

General Procedures. All reactions were carried out under an atmosphere of nitrogen. IR spectra were recorded as Nujol mulls on a Perkin-Elmer 1600 series FTIR spectrometer. NMR spectra were recorded in CD_3OD on an AC300 Bruker spectrometer. Glycol, methanol, and acetonitrile were distilled prior to use. TiO_2 (anatase, BDH general purpose reagent) and TiO_2 (rutile) were checked for purity by X-ray powder diffraction before use. $Ti(O^iPr)_4$ (Aldrich) was used as received.

Synthesis of Titanium Glycolate Complexes from $Ti(O^iPr)_4$. $Na_2Ti(C_2H_4O_2)_3{\cdot}4C_2H_6O_2$ (1). $Ti(O^iPr)_4$ (5.03 g, 17.7 mmol) was added via syringe to glycol (30 mL). Sodium hydroxide (1.45 g, 36.2 mmol) was added and the reaction mixture heated to reflux (200 °C). The 2-propanol produced during the course of the reaction and most of the glycol were removed via distillation over a period of 3 h. The white solid remaining was dissolved in methanol (10 mL). Acetonitrile (70 mL) was added slowly to the solution. Colorless crystals of **1** (6.97 g) formed overnight and were isolated and dried under vacuo. IR (Nujol mull): 605 (m), 860 (w), 882 (m), 914 (m), 1030 (w), 1060 (s), 1095 cm^{-1} (m). ^1H and ^{13}C NMR: see Results and Discussion.

$K_2Ti(C_2H_4O_2)_3{\cdot}2.5C_2H_6O_2$ (2). $Ti(O^iPr)_4$ (5.07 g, 17.8 mmol) and KOH (2.03 g, 36.2 mmol) yielded 5.54 g of **2** using the same procedure as for **1**. IR (Nujol mull): 597 (m), 881 (m), 908 (m), 1064 (s, br), 1094 cm^{-1} (m, sh). Crystals suitable for X-ray crystallographic structure determination were obtained by recrystallization from a methanol/acetonitrile mixture.^1H and ^{13}C NMR: see Results and Discussion.

Table 1. Crystallographic Data and Data Collection Parameters for **1** and **2**

	1	2
formula	$C_{14}H_{36}O_{14}Na_2Ti$	$C_{11}H_{27}O_{11}K_2Ti$
fw	522.3	461.4
space group	$C222_1$	$P2_1/n$
a, Å	9.061(2)	9.385(2)
b, Å	15.387(8)	16.916(2)
c, Å	33.340(8)	11.837(2)
β, deg	90	92.31(2)
V, Å^3	4648(3)	1877.7(6)
NREF[a]	34	32
Z	8	4
d(calcd), g·cm^{-3}	1.493	1.632
crystal size, mm^3	0.12 × 0.38 × 0.70	0.38 × 0.56 × 0.64
abs coeff, mm^{-1}	0.491	0.958
transm[b] max	0.789	
transm[b] min	0.723	
index ranges: h	0−10	0−11
k	0−18	0−20
l	0−39	−14 to 14
max 2θ, deg	50	50
no. of indep data	2306	3298
R_1,[c] %	4.30	2.62
wR_2,[c] %	9.23	6.64
no. of params	312	334
Flack x param[d]	0.02(5)	

[a] See text. [b] Empirical correction using ψ data (XEMP[6]). [c] $R_1 = \sum|F_o - F_c|/\sum F_o$ for $4\sigma(F_o)$ data. $wR_2 = (\sum(w(F_o^2 - F_c))^2/\sum(wF_o^2)^2)^{1/2}$, for all data. [d] $x = 0$ for correct configuration.[19]

Reaction of TiO_2 with Glycol. Anatase. TiO_2 (1.0 g, 12.5 mmol) and NaOH (1.0 g, 25 mmol) were suspended in glycol (40 mL). The reaction mixture was heated at 200 °C for 24 h. Most of the glycol was subsequently removed by distillation. The remaining white solid was extracted with methanol (15 mL). Addition of acetonitrile afforded colorless crystals (4.43 g) identified as pure **1**. Crystals suitable for X-ray crystallographic structure determination were obtained by recrystallization from hot glycol.

Rutile. TiO_2 (1.0 g, 12.5 mmol) and NaOH (1.0 g, 25 mmol) were suspended in glycol (40 mL). The reaction mixture was heated at 200 °C for 24 h. Most of the glycol was removed by distillation. The remaining white solid was extracted with methanol (15 mL). Unreacted TiO_2 (0.12 g) was recovered, indicating a conversion of 88%. The methanol-soluble product was identified to be **1** by IR spectroscopy.

X-ray Structure Determination of 1 and 2. Most crystallographic details are provided in Table 1. Preliminary film studies were carried out using crystals sealed in glass capillaries. The data crystals of the two salts were rapidly cut from agglomerates, or to size, and mounted on a glass fiber under a N_2 cold stream. Within a few minutes of their removal after data collection, the crystals decomposed. All data were collected with ω scans at 130 K using graphite-monochromatized Mo Kα radiation (λ 0.71073 Å) on a Siemens P3 diffractometer. Cell parameters were determined by least-squares fitting of the setting angles of NREF reflections (Table 1). Three control reflections, collected every 97 reflections, showed no significant changes.

Absorption corrections were applied to **1** analytically using ψ scan data (program XEMP[6]), but not to **2** owing to experimental difficulties, and Lorentz and polarization corrections were applied. The structures were solved by direct methods.[7] The refinement program was SHELXL-93;[8] all non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were refined with isotropic thermal parameters as follows: For **1**, the free glycol hydroxyl

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Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **1**

	x	*y*	*z*	*U*(eq)[a]
Ti(1)	501(1)	96(1)	920(1)	11(1)
Na(1)	−160(2)	3449(1)	3815(1)	15(1)
Na(2)	648(4)	0	0	19(1)
Na(3)	0	38(2)	2500	16(1)
O(1)	1394(5)	952(2)	1284(1)	13(1)
O(2)	2248(4)	400(2)	608(1)	14(1)
O(3)	−1377(4)	180(2)	1209(1)	17(1)
O(4)	−600(4)	814(2)	539(1)	14(1)
O(5)	1094(4)	−856(2)	1280(1)	13(1)
O(6)	229(5)	−870(2)	566(1)	18(1)
O(7)	1916(5)	629(3)	2079(2)	17(1)
O(8)	3779(5)	−634(3)	1604(1)	19(1)
O(9)	410(5)	2229(3)	3452(1)	19(1)
O(10)	1631(5)	666(3)	2999(1)	19(1)
O(11)	105(5)	−1167(3)	2037(1)	17(1)
O(12)	−2532(5)	−1346(3)	1468(1)	19(1)
O(13)	202(6)	2555(3)	4375(1)	25(1)
O(14)	409(6)	4324(3)	4363(1)	20(1)
C(1)	2776(7)	1306(4)	1160(2)	18(1)
C(2)	2868(7)	1214(4)	712(2)	16(1)
C(3)	−2490(7)	689(4)	1020(2)	20(1)
C(4)	−2163(7)	693(4)	575(2)	20(2)
C(5)	1217(7)	−1691(4)	1096(2)	15(1)
C(6)	171(7)	−1700(4)	739(2)	19(1)
C(7)	3436(7)	422(4)	2140(2)	16(1)
C(8)	3793(7)	−488(4)	2024(2)	19(1)
C(9)	840(8)	2170(4)	3043(2)	24(2)
C(10)	2070(7)	1548(4)	2968(2)	19(1)
C(11)	−1005(7)	−1819(4)	2033(2)	20(2)
C(12)	−2483(7)	−1492(4)	1891(2)	22(2)
C(13)	783(7)	2994(3)	4717(1)	48(2)
C(14)	197(7)	3871(3)	4727(1)	41(2)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 3. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **2**

	x	*y*	*z*	*U*(eq)[a]
Ti(1)	1222(1)	8317(1)	3147(1)	12(1)
K(1)	5187(1)	8309(1)	3152(1)	18(1)
K(2)	3306(1)	7523(1)	5805(1)	18(1)
O(1)	−78(2)	9031(1)	2323(1)	20(1)
O(2)	2587(2)	8978(1)	2476(1)	17(1)
O(3)	−414(2)	7943(1)	4016(1)	17(1)
O(4)	1517(2)	8902(1)	4551(1)	19(1)
O(5)	816(2)	7488(1)	2032(1)	15(1)
O(6)	2675(2)	7561(1)	3595(1)	14(1)
O(7)	5623(2)	8116(1)	655(1)	21(1)
O(8)	7148(2)	9173(1)	2046(1)	25(1)
O(9)	5897(2)	7126(1)	4882(1)	25(1)
O(10)	7430(2)	7294(1)	2884(1)	18(1)
O(11)	4193(2)	9027(1)	5146(1)	23(1)
C(1)	561(2)	9672(1)	1785(2)	24(1)
C(2)	2080(3)	9742(1)	2246(2)	23(1)
C(3)	−867(2)	8535(1)	4765(2)	20(1)
C(4)	461(2)	8855(1)	5363(2)	20(1)
C(5)	1404(2)	6748(1)	2304(2)	19(1)
C(6)	2839(2)	6904(1)	2886(2)	19(1)
C(7)	5543(2)	8946(1)	476(2)	20(1)
C(8)	6905(3)	9328(1)	883(2)	22(1)
C(9)	7021(3)	6612(1)	4636(2)	23(1)
C(10)	7147(3)	6559(1)	3383(2)	22(1)
C(11)	4587(3)	9806(1)	5454(2)	26(1)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

hydrogens were fully refined; the methylene hydrogens were refined in idealized riding positions, using two common group thermal parameters for the coordinated and uncoordinated glycol molecule hydrogens. For **2**, all hydrogens were fully refined. Final atomic parameters for non-hydrogen atoms are listed in Tables 2 and 3.

Results and Discussion

The reactions of titanium tetraalkoxides with bidentate chelate alkoxides such as glycol[9] or 2-methylpentane-2,4-diol[10] have been reported in the literature. The neutral compounds are characterized by various complex geometrics, which depend on the stoichiometry of the chelate diol and titanium. More recently, a number of reports described the syntheses and structures of anionic titanium alkoxides. Catechol (1,2-dihydroxybenzene) reacts with $TiCl_4$ in the presence of ammonia to form a hexacoordinate complex of the formula $[NH_4]_2Ti(cat)_3$.[11] Pentacoordinate titanium alkoxide complexes are formed in the reaction of $Ti(O^iPr)_4$ with LiO^iPr.[12] Our work shows that the reaction of $Ti(O^iPr)_4$ with 2 equiv of sodium or potassium hydroxide in an excess of glycol gives high yields of the titanium tris(glycolate) salts **1** and **2** . These compounds are highly crystalline, hygroscopic materials and crystallize as salts, solvated with varying numbers of glycol molecules.

The solid state infrared spectra of **1** and **2** are characterized by bands occurring at 605 cm^{-1} for **1** and 597 cm^{-1} for **2**, which we assign to the ν(Ti−O) stretching frequency. The ν(Ti−O) stretching frequency for $Ti(O^iPr)_4$ has previously been assigned to a band at 619 cm^{-1} and is characteristic for titanium alkoxides.[12] The bands for **1** and **2** observed between 3000 and 800 cm^{-1} are similar in position and intensity.

Compound **1** is also obtained from the reaction of crystalline TiO_2 with NaOH in glycol.

^{13}C and ^1H NMR spectra of **1** and **2** have been recorded in CD_3OD. The ^{13}C spectrum displays two broad signals at 74.1 and 63.9 ppm at room temperature which remain unchanged on lowering the temperature. The signal at 63.9 ppm was assigned to free glycol as its intensity in the NMR spectrum is reduced after removing free glycol by heating to 180 °C under high vacuum and recording the NMR spectra in CD_3OD. The signal at 74.1 ppm is assigned to chelated glycolate ligand. The reason for the broadness of the signals may be due to an exchange of bonded with free glycol. The ^1H NMR spectrum also displays broad signals at 4.3 and 3.6 ppm due to free and coordinated glycols.

There are several structural features common to both salts (see Tables 4 and 5 and Figure 1). Both have a number of hydrogen-bonded glycol molecules. The number of free glycol molecules is shown by the Experimental Section formulas. There are variations in the Ti−O bond lengths and these are related to the closeness of the cation−O contact, e.g.: Na(2)···O(6) 2.475 Å, Ti(1)−O(6) 1.915(4) Å in **1**; K(1)···O(2) 2.788 Å, Ti(1)−O(2) 1.899(2) Å in **2**. The mean Ti−O length for both structures is 1.945(22) Å. There is considerable distortion from octahedral coordination about the titanium, consistent with the narrow bite angle of the glycolate ligand (mean angle 80.2(6)°). According to the measures proposed by Muetterties and Guggenberger,[13] the distortion toward a trigonal prism is similar to that of $Fe(S_2CN(CH_2)_4)_3$[14] with for example in **1** the δ's at b_1 averaging 50.0° and at b_2 88.9° and a mean twist angle (ϕ) of 38°. The cation−oxygen distances vary over a considerable range, but the overall means of 2.41(8), 2.81(15), and 2.749(5) Å for **1**

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Scheme 1

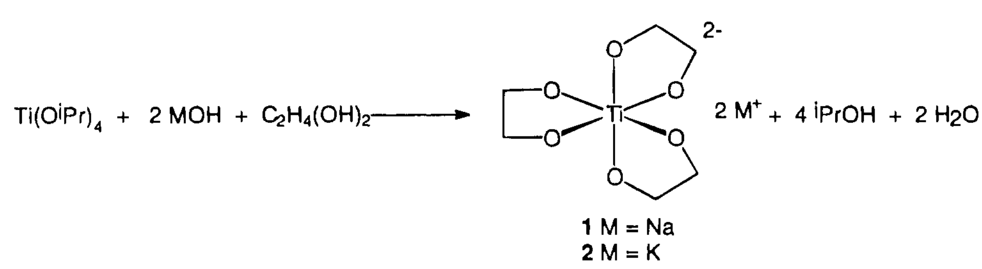

Table 4. Selected Bond Lengths (Å) and Angles (deg)

atoms	**1**	**2**
Ti(1)–O(1)	1.964(4)	1.951(2)
Ti(1)–O(2)	1.952(4)	1.899(2)
Ti(1)–O(3)	1.960(4)	1.986(2)
Ti(1)–O(4)	1.956(4)	1.945(2)
Ti(1)–O(5)	1.969(4)	1.952(1)
Ti(1)–O(6)	1.915(4)	1.928(1)
Ti–O(mean)	1.953(19)	1.943(28)
O(1)–Ti(1)–O(2)	80.5(2)	81.05(6)
O(1)–Ti(1)–O(3)	90.6(2)	88.59(6)
O(1)–Ti(1)–O(4)	103.5(2)	100.14(7)
O(1)–Ti(1)–O(5)	90.6(2)	90.33(6)
O(1)–Ti(1)–O(6)	162.6(2)	165.86(6)
O(2)–Ti(1)–O(3)	162.0(2)	162.40(6)
O(2)–Ti(1)–O(4)	86.1(2)	89.01(6)
O(2)–Ti(1)–O(5)	106.4(2)	104.86(6)
O(2)–Ti(1)–O(6)	87.8(2)	91.39(6)
O(3)–Ti(1)–O(4)	80.8(2)	78.79(6)
O(3)–Ti(1)–O(5)	89.2(2)	89.30(6)
O(3)–Ti(1)–O(6)	104.0(2)	101.50(6)
O(4)–Ti(1)–O(5)	162.7(2)	163.85(6)
O(4)–Ti(1)–O(6)	88.4(2)	91.60(6)
O(5)–Ti(1)–O(6)	80.4(2)	80.02(6)
Ti(1)–C(1)–C(1)	116.0(3)	115.82(13)
Ti(1)–O(2)–C(2)	113.8(3)	113.28(13)
Ti(1)–O(3)–C(3)	115.7(3)	110.94(13)
Ti(1)–O(4)–C(4)	112.1(3)	118.32(13)
Ti(1)–O(5)–C(5)	115.3(3)	114.94(12)
Ti(1)–O(6)–C(6)	117.3(3)	116.98(12)
O(1)–C(1)–C(2)	107.6(5)	108.1(2)
O(2)–C(2)–C(1)	107.7(5)	107.8(2)
O(3)–C(3)–C(4)	107.3(5)	106.6(2)
O(4)–C(4)–C(3)	105.9(5)	106.8(2)
O(5)–C(5)–C(6)	107.3(5)	106.5(2)
O(6)–C(6)–C(5)	106.8(5)	107.1(2)

Table 5. Selected Dihedral Angles (deg)

atoms	**1**	**2**[a]
Ti(1)–O(1)–C(1)–C(2)	23.5(6)	14.2(2)
Ti(1)–O(2)–C(2)–C(1)	39.1(6)	41.1(2)
Ti(1)–O(3)–C(3)–C(4)	24.8(6)	46.6(2)
Ti(1)–O(4)–C(4)–C(3)	43.8(6)	16.5(2)
Ti(1)–O(5)–C(5)–C(6)	−27.4(5)	36.4(2)
Ti(1)–O(6)–C(6)–C(5)	−34.3(6)	28.3(2)
O(1)–C(1)–C(2)–O(2)	−38.9(7)	−34.3(3)
O(3)–C(3)–C(4)–O(4)	−42.8(6)	−39.5(2)
O(5)–C(5)–C(6)–O(6)	37.5(6)	−39.7(2)

[a] Angles given for the centosymmetrically related molecule in **2** for easier comparison.

and **2** are consistent with the ionic radii of Na$^+$ and K$^+$, respectively.

Structure **1** contains a single enantiomer of Δ chirality. Figure 1 illustrates the Δ form of **2**, arbitrarily chosen from the two possible molecules in the centrosymmetric cell. The C_3-symmetric axis is approximate in **2**. The glycolato carbons adopt a nonsymmetric λλδ conformation in **1** and λλλ in **2**; the configurations are therefore, for **1**, Δ(λλδ) and, for **2**, Δ(λλλ) + Λ(δδδ).

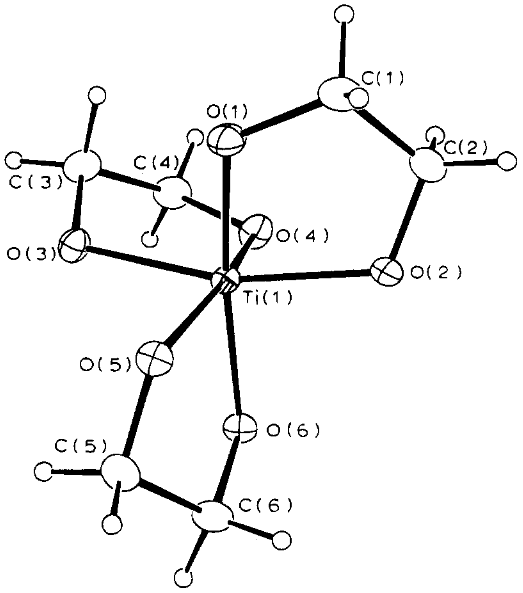

Figure 1. Molecular structure and atom numbering of the anionic part of $K_2Ti(C_2H_4O_2)\cdot 2.5C_2H_6O_2$ (**2**) with 30% probability thermal ellipsoids. For selected bond lengths and angles see Tables 4 and 5.

The molecular packing interactions are a combination of hydrogen bonds between glycol molecules and the coordinated oxygens (H···O 1.81–2.10 Å) and the ionic contacts between the cations and both the coordinated and free glycolato oxygens. The sodium cations in **1** have five or six and the potassium cation in **2** has seven close ion contacts.

There are few examples of similar titanium(IV) anions reported in the literature, though a wide range of Ti–O bond lengths, frequently involving bridging oxygen atoms in polymeric compounds, has been observed.[15–18] There are no anomalous bond lengths or angles in the structures of **1** and **2**.

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Supplementary Material Available: Listings of anisotropic thermal parameters, H atom coordinates, nonessential bond lengths and angles for **1** and **2** (6 pages). Ordering information is given on any current masthead page.

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