Structural Chemistry of Titanium Alkoxides Substituted by the Chelating Bidentate Ligands Isoeugenolate or 2-Aminoethanolate

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Dedicated to Professor Hubert Schmidbaur on the occasion of his 70th birthday

The compounds [Ti(OPr)$_3$(isoeugenolate)]$_2$ and [Ti(OR)$_3$(OCH$_2$CH$_2$NH$_2$)]$_2$(R = ^{i}Pr, Et), obtained by reaction of titanium alkoxides with isoeugenol (2-methoxy-4-propenylphenol) or 2-aminoethanol, are centrosymmetric dimers with a central Ti$_2$(μ_2-OR)$_2$ unit. The isoeugenolate and 2-aminoethanolate ligands are chelating, with the uncharged donor group (OR or NH$_2$, respectively) axial to the Ti$_2$(μ_2-OR)$_2$ ring.

Key words: Titanium Alkoxide Derivatives, Chelating Ligands, Organically Modified Metal Alkoxides

Introduction

Unlike silicon alkoxides, Si(OR)$_4$, which are always monomeric and unsolvated, Ti(OR)$_4$, (and metal alkoxides in general) have a high tendency to increase their coordination numbers. In the absence of an external Lewis base the coordination number is increased by aggregation to larger units *via* alkoxo bridges. The degree of association depends on the steric bulk of the alkoxo ligands. For example, the titanium atoms in the tetramer [Ti(OR)$_4$]$_4$ (R = Me, Et) reach their optimal coordination number of 6 by formation of two μ_3-OEt and four μ_2-OEt ligands [1], while Ti(OCH$_2$^{t}Bu)$_4$ is only dimeric with five-coordinate titanium [2].

When the metal alkoxides are dissolved in polar solvents, addition of the solvent molecules competes with association and reduces the degree of association. The alkoxides M(O^{i}Pr)$_4$ (Zr [3], Hf [3, 4]) crystallize from isopropanol as M$_2$(O^{i}Pr)$_8$(^{i}PrOH)$_2$, where each metal atom is six-coordinate owing to both the formation of alkoxide bridges and coordination of alcohol molecules (Scheme 1). The same structure type was found for several crystalline Ti(OR)$_4$ compounds with fluorinated alkoxo or arlyoxo ligands [5]; the alcohol solvate Ti(OEt)$_4$(EtOH) was only observed in solution at low temperature [6]. Secondary amines can be coordinated in the same way; several isostructural amine adducts were recently structurally characterized [7].
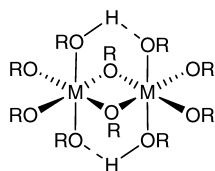
Scheme 1. Schematic structure of M$_2$(OR)$_8$(ROH)$_2$ (M = Ti, Zr, Hf).

Titanium alkoxides react spontaneously with water and form precipitates rather than gels. The most general method to moderate the hydrolysis and condensation reactions is to substitute one or more alkoxide groups by bidentate (chelating or bridging) ligands. The reactivity of the thus obtained modified precursors is lower because the bidentate ligands block coordination sites at the metal [8]. Various bi- and multidentate ligands have been used for this purpose, but only few compounds were structurally characterized.

The structurally characterized derivatives with anionic chelating bidentate ligands (X∩Y), *viz.* [Ti(OEt)$_3$(glycinate)]$_2$ [9], several [Ti(OR)$_3$(β-diketonate)]$_2$ derivatives [10] and [Ti$_2$(OR)$_6$(DHP)]$_2$ (DHP = dianion of 4,6-dihydroxypyrimidine) [11], are related to the M$_2$(OR)$_8$L$_2$ (L = neutral ligand) structure type. In the compounds [Ti(OR)$_3$(X∩Y)]$_2$ (Scheme 2) the chelating ligands occupy the coordination sites of the neutral ligand and a terminal alkoxide. The coordinated nitrogen donor group of the glycinate or DHP derivative is in the X position, *i.e.* the same
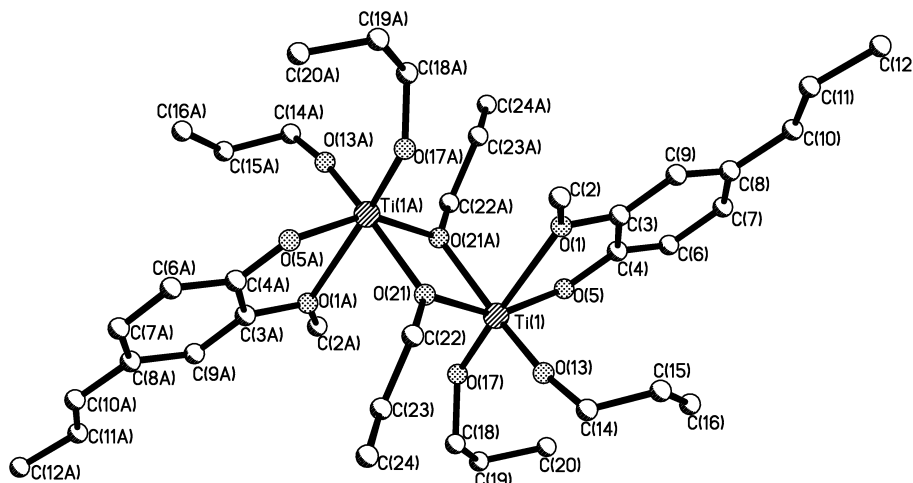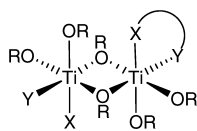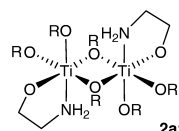
Fig. 1. Molecular structure of [Ti(OPr)₃(isoeugenolate)]₂ (**1**).

Scheme 2. Schematic structure of [Ti(OR)₃(X∩Y)]₂ (X∩Y = anionic chelating bidentate ligand).

position as the coordinated alcohol in $M_2(OR)_8L_2$ (L = ROH or RNH_2). In this paper, we report the structure analyses of two other derivatives with similar structures, *viz.* [Ti(OPr)₃(isoeugenolate)]₂ (**1**) and [Ti(OR)₃(OCH₂CH₂NH₂)]₂ (**2a**: R = ^{i}Pr; **2b**: R = Et).

Results and Discussion

We have previously prepared Ti(O^{i}Pr)₃(isoeugenolate) by the reaction of Ti(O^{i}Pr)₄ with isoeugenol (2-methoxy-4-propenylphenol) [12]. This derivative was spectroscopically characterized and used for the preparation of sol-gel materials with polymerizable organic groups. We were now able to obtain crystals of the *n*-propyl derivative [Ti(OPr)₃(isoeugenolate)]₂ (**1**). The results of the X-ray structure analysis (Fig. 1) confirm our previous structural proposal, based on the spectroscopic results, that the isoeugenolate ligand is bonded to the titanium atom as a chelating ligand. This

1

explains why the isoeugenolate ligand, although being an aryloxo derivative, is less easily hydrolyzed than the OPr ligands. Although isoeugenol was employed for the synthesis of **1** that contained about 9% of the *syn* isomer, only the isomer with the *anti* propenyl group was found in two independent crystal structure analyses.

Compounds of the same structure type were obtained when Ti(OEt)₄ or Ti(O^{i}Pr)₄ was reacted with 2-aminoethanol. The reaction is straightforward when one equivalent of 2-aminoethanol is used; however, **2** crystallized more readily when an excess of Ti(OR)₄ was used. N-Alkylaminoethanolate derivatives of titanium alkoxides were previously prepared [13] but not structurally characterized. The molecular structure of the *iso*-propoxy derivative **2a** is shown in Fig. 2, the ethoxy derivative **2b** is isostructural.

Both **1** and **2a** are centrosymmetric dimers, and their structures correspond to the general structure type shown in Scheme 2 with the neutral OMe or NH₂ groups axial to the Ti₂(μ_2-OR)₂ plane. The asymmetric unit of **1** contains two halves of the molecule; both have nearly identical structural parameters. The corresponding bond distances and angles in **1** and **2a** are rather similar and are compared with each other in Table 1. The bond distances of both the bridging and the terminal OR ligands are influenced by the corresponding *trans* ligand; the shortest Ti-OR distance is that
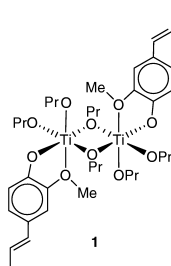
1: Molecule 1		1: Molecule 2		2a	
Ti(1)-O(21)	200.2(3)	Ti(2)-O(37)	199.4(3)	Ti(1)-O(1)	201.6(2)
Ti(1)-O(21)*	204.9(3)	Ti(2)-O(37)*	205.6(3)	Ti(1)-O(1)*	209.2(2)
Ti(1)-O(13)	177.3(3)	Ti(2)-O(41)	177.5(4)	Ti(1)-O(4)	181.2(2)
Ti(1)-O(17)	178.1(3)	Ti(2)-O(45)	178.7(3)	Ti(1)-O(3)	185.3(2)
Ti(1)-O(5)	191.6(3)	Ti(2)-O(29)	192.1(3)	Ti(1)-O(2)	187.8(2)
Ti(1)-O(1)	238.6(3)	Ti(2)-O(25)	238.0(3)	Ti(1)-N(1)	229.8(3)
O(21)-Ti(1)-O(21)*	71.4(1)	O(37)-Ti(2)-O(37)*	71.6(1)	O(1)-Ti(1)-O(1)*	74.03(9)
O(1)-Ti(1)-O(5)	72.1(1)	O(25)-Ti(2)-O(29)	72.1(1)	N(1)-Ti(1)-O(2)	77.5(1)
O(1)-Ti(1)-O(17)	169.5(1)	O(25)-Ti(2)-O(45)	169.3(1)	N(1)-Ti(1)-O(3)	172.6(1)
O(17)-Ti(1)-O(21)	104.8(1)	O(45)-Ti(2)-O(37)	104.9(2)	O(3)-Ti(1)-O(1)	97.3(1)
O(17)-Ti(1)-O(21)*	94.3(1)	O(45)-Ti(2)-O(37)*	94.2(2)	O(3)-Ti(1)-O(1)*	90.94(9)
O(1)-Ti(1)-O(21)	84.1(1)	O(25)-Ti(2)-O(37)	84.8(1)	N(1)-Ti(1)-O(1)	83.16(9)
O(1)-Ti(1)-O(21)*	83.3(1)	O(25)-Ti(2)-O(37)*	84.3(1)	N(1)-Ti(1)-O(1)*	82.08(9)
O(17)-Ti(1)-O(13)	99.8(2)	O(45)-Ti(2)-O41)	99.7(2)	O(3)-Ti(1)-O(4)	98.2(1)
O(13)-Ti(1)-O(21)*	161.4(2)	O(41)-Ti(2)-O(37)*	161.9(2)	O(4)-Ti(1)-O(1)*	167.6(1)
Ti(1)-O(21)-Ti(1)*	108.7(1)	Ti(2)-O(37)-(Ti2)*	108.4(1)	Ti(1)-O(1)-Ti(1)*	105.97(9)

Table 1. Selected bond distances and angles in **1** and **2a**. Corresponding values are given in the same line.
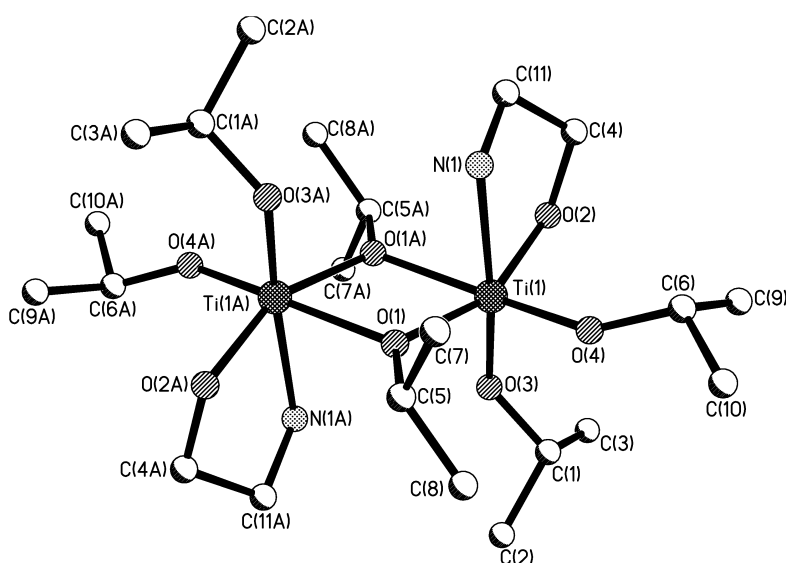
* Inversion related atoms.

Fig. 2. Molecular structure of $[Ti(O^iPr)_3(OCH_2CH_2NH_2)]_2$ (**2a**).

trans to the bridging alkoxo group (O(13) and O(41) in **1**, and O(4) in **2a**), and the longest that of the bridging alkoxo group *trans* to the terminal OR ligand (O(21)* and O(37)* in **1**, and O(1)* in **2a**).

The crystallographic symmetry places the neutral donor atoms (OMe in **1** and NH_2 in **2**) in a mutual *trans* position relative to the $Ti_2(\mu_2\text{-}OR)_2$ ring. Note that no hydrogen bridges are possible in **1** that might stabilize this arrangement as in $M_2(OR)_8(ROH)_2$. In **2a**, the rather long N···O distance (N(1)···O(3)* 310.9(3) pm) also indicates the absence of significant intramolecular hydrogen bonding. For comparison: the N···O distance in $Ti_2(O^iPr)_8(PrNH_2)_2$ is 295.2(2) [7]. Both **1** and **2a** show a slight tetrahedral distortion due to the chelate ligand and the $Ti_2(\mu_2\text{-}OR)_2$ core; for ex-

ample, the angle between the terminal OR groups is increased as well as the average angle between the terminal OR groups and the ring atoms.

When crystalline **1** was dissolved in CD_2Cl_2 and cooled down to −60 °C, more signals were observed in the NMR spectra than expected from the molecular symmetry in the crystalline state. Similar phenomena were observed for **2**. The low temperature NMR spectra thus could be an indication that a *cis-trans* equilibrium (*i.e.*, the neutral donor atoms *cis* or *trans* relative to the $Ti_2(\mu_2\text{-}OR)_2$ ring) exists in solution.

Conclusions

The substitution of one OR ligand in titanium alkoxides $Ti(OR)_4$ by an anionic chelating bidentate ligand

X∩Y results in derivatives of the type Ti(OR)$_3$(X∩Y). These compounds have a high tendency for dimerization *via* alkoxo bridges that allows each titanium atom to reach the preferred coordination number of six. The solid-state structures of the isoeugenolate derivative **1** and the 2-aminoethanolate derivatives **2** are variations of the general structure type M$_2$(μ_2-OR)$_2$(μ_1-OR)$_4$L$_2$ observed in many alkoxo derivatives of the tetravalent metals. In **1** and **2**, the ligands L are represented by the neutral donor groups of the chelating ligands, *viz.* OMe in **1** and NH$_2$ in **2**. Both compounds are of the type Ti(OR)$_3$(O∩X) where the negatively charged oxygen atom (of an aryloxo, alkoxo, carboxylate or β-diketonate group, respectively) substitutes an OR$^-$ ligand of the parent titanium alkoxide and the second (uncharged) donor atom (OMe, NH$_2$, C=O, *etc.*) coordinates in an axial position relative to the Ti$_2$(μ_2-OR)$_2$ core (in the case of the β-diketonate ligands this generalization is rather formal).

Experimental Section

All operations were carried out in a moisture- and oxygen-free argon atmosphere using the Schlenk technique. All solvents were dried by standard methods.

Synthesis of [Ti(OPr)$_3$(isoeugenolate)]$_2$ (**1**)

An amount of 376 mg (2.29 mmol) isoeugenol (2-methoxy-4-propenylphenol, Aldrich, 98%, mixture of 9.4% *syn* and 90.6% *anti* isomers) was added dropwise to 788 mg (2.01 mmol) Ti(OPr)$_4$ (Aldrich, 98%) under stirring (without a solvent). Orange crystals were obtained from the red solution after 10 d. The crystals were isolated by decantation, washed with several portions of propanol at −70 °C and dried at $4 \cdot 10^{-4}$ mbar for 10 h. Yield 295 mg (38%). ^{1}H NMR (300.13 MHz, CD$_2$Cl$_2$, 20 °C): δ = 6.93 − 6.78 (m, 4 H, Ar^{3,5}), 6.62 (d, J_{HH} = 8.1 Hz, 2 H, Ar^6), 6.32 (dd, J_{HH} = 15.7 Hz, J_{HH} = 1.6 Hz, 2 H, H^7), 6.05 (dq, J_{HH} = 15.7 Hz, J_{HH} = 6.5 Hz, 2 H, H^8), 4.45 (t, J_{HH} = 6.6 Hz, 12 H, OCH_2), 3.88 (s, 6 H, CH_3^{10}), 1.86 (dd, J_{HH} = 6.5 Hz, J_{HH} = 1.6 Hz,
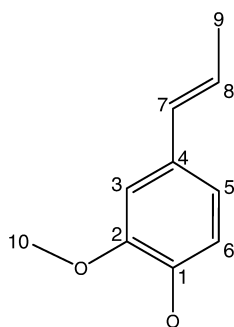
6 H, CH_3^{9}), 1.70 − 1.51 (m, 12 H, CH$_3$CH_2), 0.97 − 0.88 (m, 18 H, CH$_2$CH_3). − ^{13}C{^{1}H} NMR (75.47 MHz, CD$_2$Cl$_2$, 20 °C): δ = 153.5 (C^1), 149.4 (C^2), 130.8 (C^7), 129.0 (C^4), 122.7 (C^8), 120.8 (C^3), 114.1 (C^5), 106.8 (C^6), 80.0 (OCH$_2$), 56.8 (C^{10}), 26.4 (CH$_3$CH$_2$), 18.1 (C^9), 10.0 (CH$_2$CH$_3$).

Preparation of Ti$_2$(O^{i}Pr)$_6$(O(CH$_2$)$_2$NH$_2$)$_2$ (**2a**)

An amount of 1.90 g (6.68 mmol) of Ti(O^{i}Pr)$_4$ (Aldrich 97%, used as received) was dissolved at room temperature in 2 ml of *n*-heptane in a Schlenk tube. Then 0.18 g (2.91 mmol) of 2-aminoethanol (Aldrich 99.5+%, used as received) was added dropwise under stirring. The solution was then concentrated until the compound precipitated. The amorphous solid was dissolved in 1 ml of toluene under heating until a clear solution was obtained. The vessel was then stored at 4 °C to afford colorless crystals after 3 h. The solvent was decanted and the product was dried *in vacuo*. Yield 0.62 g (75%, rel. aminoethanol). ^{1}H NMR (300.13 MHz, CD$_2$Cl$_2$, 20 °C): δ = 4.81, 4.75, 4.51 (br, 6 H, OCH(CH$_3$)$_2$), 4.20 (b, 4 H, OCH_2CH$_2$NH$_2$), 4.00 (b, HOCH(CH$_3$)$_2$), 3.04 (b, 4 H, NH$_2$CH_2CH$_2$O), 1.37 − 1.24 (m, 36 H, OCH(CH_3)$_2$). − ^{13}C{^{1}H} NMR (75.47 MHz, CD$_2$Cl$_2$, 20 °C): δ = 76.27, 75.83, 75.47 (OCH(CH$_3$)$_2$), 72.01 (OCH$_2$CH$_2$NH$_2$), 64.29 (HOCH(CH$_3$)$_2$), 44.93 (NH$_2$CH$_2$CH$_2$O), 29.66, 26.20, 24.25 (OCH(CH$_3$)$_2$).

Compound **2b** was prepared analogously.

X-ray structure analyses

Selected crystals were mounted on a Siemens SMART diffractometer with a CCD area detector. Graphite-monochromated Mo-K$_\alpha$ radiation (71.073 pm) was used for all measurements. The crystal-to-detector distance was 5.0 cm. A hemisphere of data was collected by a combination of three sets of exposures at 173 K. Each set had a different ϕ angle for the crystal, and each exposure took 20 s and covered 0.3° in ω. The data were corrected for polarization and Lorentz effects, and an empirical absorption correction (SADABS) was applied. The cell dimensions were refined with all unique reflections (Table 2). The structure was solved by the Patterson method (SHELXS97). Refinement was carried out with the full-matrix least-squares method based on F^2 (SHELXL97) with anisotropic displacement parameters for all non-hydrogen atoms. Hydrogen atoms were inserted in calculated positions and refined riding with the corresponding atom. Crystallographic data (excluding structure factors) have been deposited at the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 245538 (**1**), CCDC 245539 (**2a**), CCDC 245540 (**2b**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223/336033; E-mail: deposit@ccdc.cam.ac.uk).

	1	**2a**	**2b**
Empirical formula	$C_{38}H_{64}O_{10}Ti_2$	$C_{22}H_{54}N_2O_8Ti_2$	$C_{16}H_{42}N_2O_8Ti_2$
Formula weight	776.7	570.5	486.3
Crystal system, space group	triclinic, $P\text{-}1$	monoclinic, $P2_1/c$	hexagonal, $R\text{-}3$
a [pm]	999.27(7)	1168.6(2)	2321.6(3)
b [pm]	1305.72(9)	1320.4(2)	
c [pm]	1729.7(1)	1089.9(1)	1368.7(3)
α [deg]	72.008(2)		
β [deg]	89.339(2)	115.600(3)	
γ [deg]	81.167(2)		
Volume [pm^3]	$2119.5(3)\cdot10^6$	$1516.7(3)\cdot10^6$	$6388(2)\cdot10^6$
Z / Calcd. density [$g\cdot cm^{-3}$]	2 / 1.217	2 / 1.249	9 / 1.138
μ [mm^{-1}]	0.427	0.568	0.596
Crystal size [mm]	$0.28\times0.17\times0.10$	$0.76\times0.56\times0.35$	$0.75\times0.59\times0.32$
θ Range	$2.36-25.00$	$2.47-25.00$	$2.51-25.00$
Reflections coll. / unique	11705 / 7416	4610 / 1767	8607 / 2314
Data / parameters	7416 / 452	1767 / 194	2314 / 131
GOF	1.021	0.911	1.048
$R_1[I>2\sigma(I)]$, wR_2	0.0778, 0.1674	0.0470, 0.1071	0.0828, 0.2310
R_1 (all data), wR_2	0.1297, 0.1867	0.0596, 0.1102	0.1029, 0.2480
Largest diff. peak and hole [$e\cdot\mathring{A}^{-3}$]	0.478 / -0.478	0.441 / -0.205	1.865 / -0.786*

Table 2. Crystallographic and structural parameters of **1** and **2**.

* The residual electron density is rather high due to disordered ethanol located along the -3 axis.

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