

Note

A binaphtholate titanium complex featuring a linear tetradentate [OSSO]-bis(phenolato) ligand: Synthesis and partial hydrolysis to a homochiral dinuclear complex

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Abstract

Reaction of $[(R)\text{-C}_{20}\text{H}_{12}\text{O}_2]\text{Ti}(\text{O}^i\text{Pr})_2$ with 1,4-dithiaalkanediy-2,2'-bis(6-*tert*-butyl-4-methyl-phenol) affords the chiral-at-metal complex $[(R)\text{-C}_{20}\text{H}_{12}\text{O}_2]\text{Ti}\{(\text{C}_6\text{H}_2\text{O}-^i\text{Bu}-6\text{-Me}-4)_2\text{S}(\text{CH}_2)_2\text{S}\}$ (**1**) in low diastereomeric excess. Complex **1** can be partially hydrolyzed to give a dinuclear species $[\mu\text{-}\{(R)\text{-C}_{20}\text{H}_{12}\text{O}_2\}\text{-}\mu\text{-O}\text{-}\{(A)\text{-Ti}\{(\text{C}_6\text{H}_2\text{O}-^i\text{Bu}-6\text{-Me}-4)_2\text{S}(\text{CH}_2)_2\text{S}\}}_2]$ (**2**), in which the two titanium centers are homochiral. The molecular structure of **1** and **2** was confirmed by single crystal X-ray analysis, which shows C_2 -symmetry in both complexes.

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1. Introduction

A good understanding of the molecular mechanism and the origin of stereoselectivity in the polymerization of α -olefins has led to the rational design of new highly active and selective metallocene and post-metallocene catalysts [1,2]. However, for polymerization of styrene the relation between catalyst structure and its polymerization properties remains less clear [3]. While styrene can be efficiently polymerized syndiotactically by titanium(III) half-sandwich complexes of the type $[\text{Ti}(\eta^5\text{-C}_5\text{R}_5)\text{R}']^+$ [4], examples of early transition metal-based homogeneous catalysts for the production of isotactic styrene have only been reported by Arai and coworkers [5].

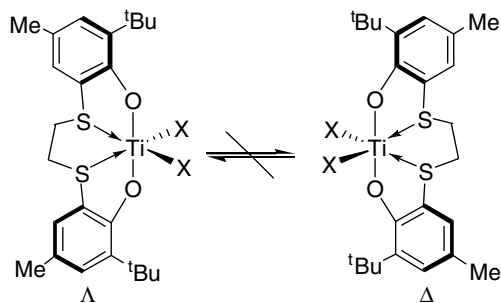
Recently, our group has introduced a series of group 4 metal catalysts bearing 1, ω -dithiaalkanediy-bridged bis(phenolato) [OSSO] ligands, some of which are able to isospecifically polymerize styrene [3,6]. It was found that the stereoregularity of the polystyrene depends greatly on

the size of the *ortho*-substituent of the phenol moiety. If insufficient in size (smaller than ^{*i*}Bu), syndiotactic polystyrene is obtained or tacticity is lost entirely [3]. An additional important factor is the length of the bridge [6]. Sulfur-bridged systems produce mainly syndiotactic polystyrene; 1,3-propanediy-bridged systems are conformationally fluxional and therefore lack the C_2 -symmetry and inherent chirality of 1,2-ethanediy-bridged complexes that is presumably necessary for isospecific styrene polymerization. The conformational stability of the 1,2-ethanediy-bridged ligand appears to be a key factor in this process and is therefore the subject of our current research efforts (Scheme 1). Group 4 metal complexes bearing this ligand adopt helical (*cis*- α) chirality [7].

In order to better study the conformational stability of these chiral complexes access to their enantiomers is desirable. Besides their use in mechanistic studies, enantiopure bis(phenolato) complexes of the type LMX_2 or LMR_2 can potentially be used in asymmetric catalysis [8]. To achieve resolution of these complexes, stereoselective complexation of the bis(phenol) to the metal center was attempted by employing a ligand that can serve as a chiral

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Scheme 1.

template. For this purpose we chose 1,1'-bi-2-naphthol (BINOL), because of its availability and its ease of functionalization [9]. Widely used as a catalyst in asymmetric transformations, $[\{(R)-C_{20}H_{12}O_2\}Ti(O^iPr)_2]$ occurs as a monomer, dimer or trimer, depending on the substitution of the BINOL [10].

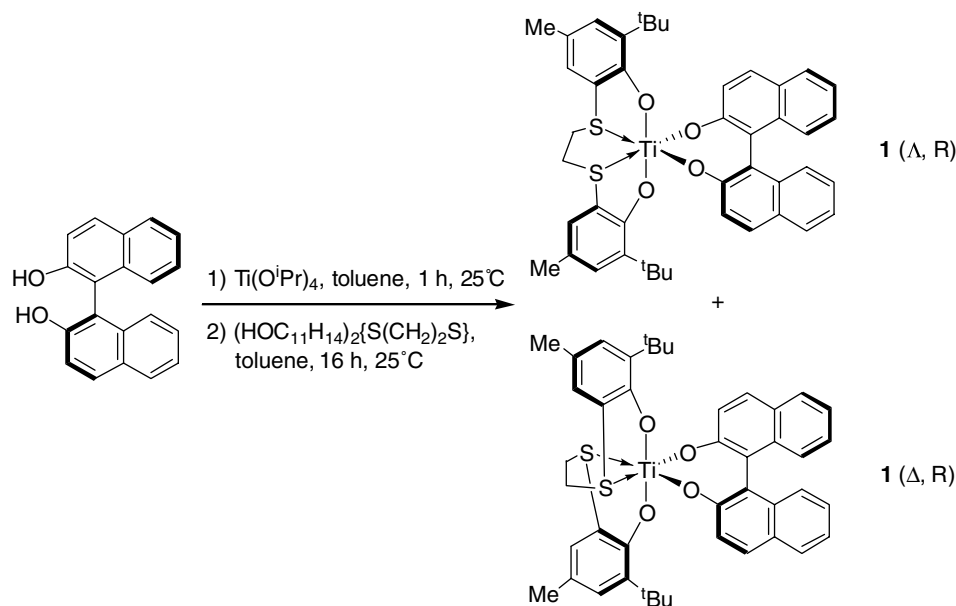
2. Results and discussion

Complex $[\{(R)-C_{20}H_{12}O_2\}Ti(O^iPr)_2]$ is accessible in high yield by reaction of $Ti(O^iPr)_4$ with (R)-BINOL [10a]. Subsequent reaction with 1,4-dithiaalkanediy-2,2'-bis(6-*tert*-butyl-4-methyl-phenol) in toluene at room temperature leads to the formation of $[\{(R)-C_{20}H_{12}O_2\}Ti\{(C_6H_2O-tBu-6-Me-4)_2S(CH_2)_2S\}]$ (**1**) as an orange-red powder (Scheme 2). Two sets of product resonances in the 1H and ^{13}C NMR spectra ($CDCl_3$) suggest the formation of two diastereomeric products in a ratio of 1:2. Complexation of the [OSSO] ligand therefore proceeds with low diastereoselectivity. In the 1H NMR spectrum, the methylene protons in the backbone of the bis(phenolate) ligand appear as AA'BB' doublets at 3.10 and 2.60 ppm with $^2J_{HH} =$

10.6 Hz. The six binaphthoxy resonances and the single resonances observed for the *tert*-butyl- and *para*-methyl substituents in the 1H NMR spectrum for each diastereomer support the formation of a C_2 -symmetrical species. Separation of the diastereomers of **1** by fractional crystallization proved to be unsuccessful despite attempts from a range of solvents. Reaction with sterically more encumbered 3,3'-substituted BINOLs ($R = Me, SiMe_3$) to improve the efficacy of the chiral template did not afford the desired products [9b].

However, single crystals suitable for X-ray analysis could be grown from diethyl ether solution at $-30^\circ C$ in which the (R, Λ)-diastereomer of **1** cocrystallizes with two crystallographically independent molecules of a second product (**2**) (vide infra). The ORTEP diagram for **1** and selected bond lengths and bond angles are shown in Fig. 1. The results confirm the formation of a C_2 -symmetric chiral complex with a *cis*- α configuration in the solid state. Bond parameters for the bis(phenolate) ligand are within the range commonly observed for this type of octahedral complexes [6]. The Ti–O bond distances for the binaphthoxy moiety (1.835(8)–1.848(7) Å) are much shorter than the Ti–Cl bonds in comparison to the analogous bis(phenolate) titanium dichloride (2.25 Å) [3,6d]. The reduced bond distance and smaller bite angle ($O3-Ti-O4 = 96.8(3)^\circ$ versus $Cl-Ti-Cl = 103.4(1)^\circ$) forces O1 and O2 in the axial positions to bend away more from their ideal octahedral positions ($O1-Ti-O2 = 153.8(3)^\circ$ versus $O-Ti-O = 156.7(2)^\circ$).

A solution of **1** in acetone did afford single crystals suitable for X-ray analysis after 24 h at $25^\circ C$. The results showed the formation of a dinuclear complex $[\mu-\{(R)-C_{20}H_{12}O_2\}-\mu-O-\{Ti\{(C_6H_2O-tBu-6-Me-4)_2S(CH_2)_2S\}\}_2]$ (**2**), in which one binaphthoxy group and an oxygen atom bridge two bis(phenolate) titanium fragments. Most likely, this



Scheme 2.

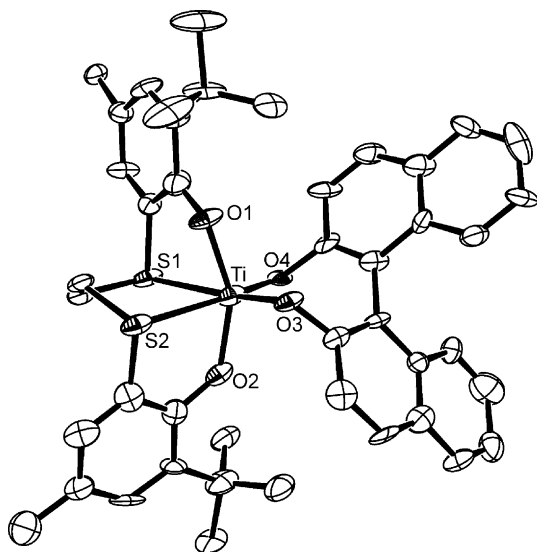


Fig. 1. ORTEP diagram of complex **1**. Hydrogen atoms are omitted for clarity. Atoms are drawn at 50% probability level. Selected bond lengths (Å) and angles (°): Ti–O1 1.895(7), Ti–O2 1.856(7), Ti–O3 1.848(7), Ti–O4 1.835(8), Ti–S1 2.691(3), Ti–S2 2.654(4), O1–Ti–O2 153.8(3), O3–Ti–O4 96.8(3), S1–Ti–S2 79.73(11).

product is formed by partial hydrolysis of **1** by H₂O present in the solvent (Scheme 3). Complex **2** can also be obtained directly from the crude reaction mixture without isolation of **1**. The high yield (80%) of the reaction exceeds the theoretical maximum that can be expected for a 1:2 diastereomer mixture. This implies the possibility of inversion of the chirality at the metal center to form a thermodynamically favored diastereomer [11].

The ¹H NMR spectrum shows six binaphthoxy resonances, indicative of C₂-symmetry of the complex in solution. The presence of two different bridging ligands renders both the *tert*-butyl and methyl substituents of each [OSSO] ligand inequivalent, which is confirmed by the presence of two *tert*-butyl and two methyl resonances in the ¹H NMR spectrum (CD₂Cl₂). The protons in the bis(phenolate) backbone are all inequivalent and appear as ABCD double doublets around 2.85 and 2.20 ppm with ²J_{HH} ≈ ³J_{HH-anti} ≈ 13–14 Hz and ³J_{HH-gauche} ≈ 2.5 Hz.

The unit cell of the crystal contains three crystallographically independent molecules. All five molecules of **2** in both crystals are closely related in structure. The titanium

atoms in these molecules are in distorted octahedral environments. An ORTEP diagram for **2** and selected bond lengths and bond angles are shown in Fig. 2. Noteworthy features of this structure are its large bond angles at the oxygen atoms of the binaphthoxy ligand and at the oxygen bridge (values vary between 141.6(4)–154.0(6)° and 143.9(3)–146.0(4)°, respectively), which suggest a strong Ti–O π-interaction [12,13]. The steric requirements of the binaphthoxy–Ti₂–O framework force the [OSSO] ligands to bend away slightly, which leads to a decrease in bond angle between the metal center and the axial bis(phenolate) oxygen atoms to 151–154°. Additionally, the two phenolate–Ti–phenolate axes are not entirely aligned in the solid state. Surprisingly, it can be observed from both crystal structures that the bis(phenolate) ligands all display the same conformation, which results in an optically active complex ([α]_D²³ = +631.2°, CH₂Cl₂) with exclusively Λ-chirality at the titanium centers. High optical rotation is commonly observed for related binaphthoxy complexes [14].

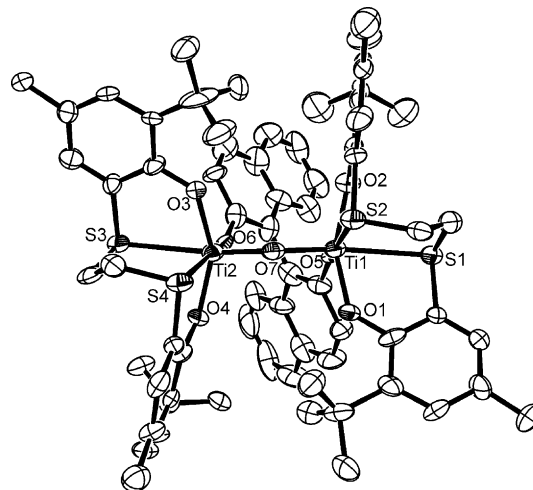
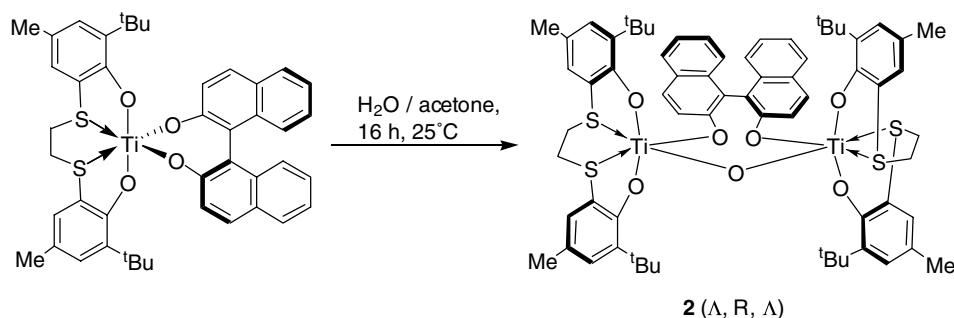


Fig. 2. ORTEP diagram of complex **2**. Only one of the crystallographically independent molecules is shown. Hydrogen atoms are omitted for clarity. Atoms are drawn at 50% probability level. Selected bond lengths (Å) and angles (°): Ti1–O1 1.917(5), Ti1–O2 1.907(5), Ti1–O5 1.815(5), Ti1–O7 1.799(5), Ti1–S1 2.711(3), Ti1–S2 2.696(3), Ti2–O3 1.894(5), Ti2–O4 1.887(5), Ti2–O6 1.812(5), Ti2–O7 1.815(5), Ti2–S3 2.711(3), Ti2–S4 2.684(2) and O1–Ti1–O2 153.2(2), S1–Ti1–S2 78.36(7), O5–Ti1–O7 102.8(2), O3–Ti2–O4 151.3(2), S3–Ti2–S4 80.00(8), O6–Ti2–O7 102.5(2), Ti1–O7–Ti2 143.9(3).



Scheme 3.

In summary, we have demonstrated the synthesis of a chiral (binaphthoxy)titanium bis(phenolate) complex. Upon hydrolysis, this species can be stereoselectively transformed into a chiral dinuclear binaphthoxy-bridged complex, which is notably homochiral at titanium.

3. Experimental

3.1. General considerations

All experiments were performed under an inert atmosphere of argon using standard Schlenk-line and glovebox techniques. Diethyl ether and THF, benzene and toluene were distilled from sodium benzophenone ketyl; pentane and hexane were distilled from sodium/triglyme benzophenone ketyl; dichloromethane was distilled from calcium hydride; acetone was used as received. (R)-(+)-1,1'-bi-2-naphthol was purchased from Acros and used as received. Titanium tetra(isopropoxide) was purchased from Aldrich, distilled and stored under argon prior to use. [(R)-(+)-1,1'-bi-2-naphthoxy]diisopropoxytitanium, 1,4-dithiabutenediyl-2,2'-bis(6-tert-butyl-4-methylphenol) and 3-tert-butyl-2-hydroxy-5-methyl-benzenethiol were synthesized following published procedures [6a,10e,15]. NMR spectra were recorded on Varian Gemini 200 and Varian Unity 500 spectrometers at 25 °C, unless otherwise stated. Chemical shifts for ¹H NMR and ¹³C NMR spectra were reported in ppm relative to tetramethylsilane, using the residual solvent resonance as internal reference. Deuterated solvents were dried over calcium hydride or sodium and degassed prior to use.

3.2. [(R)-(+)-1,1'-Bi-2-naphthoxy {1,4-dithiabutenediyl-2,2'-bis(6-tert-butyl-4-methylphenoxy)}titanium] (1)

To [(R)-C₂₀H₁₂O₂]Ti(OⁱPr)₂] (0.302 g, 0.67 mmol) was added a solution of (HOC₆H₂-^tBu-6-Me-4)₂S(CH₂)₂S} (0.279 g, 0.67 mmol) in 15 mL of toluene at 25 °C. An additional 20 ml of toluene was added and the mixture was stirred overnight at the same temperature, after which the volatiles were removed in vacuo. The resulting oily red solid was washed with pentane and subsequently dried. An orange powder was obtained by diffusion of pentane into a toluene solution of the product; yield 0.212 g (43%). Single crystals suitable for X-ray analysis could be obtained from Et₂O solution at -30 °C after several months. These red crystals consisted of cocrystallized **1** and **2**. *Diastereomer 1 (major)*: ¹H NMR (CDCl₃): 7.74 (d, ³J_{HH} = 8.1 Hz, 2H, naphth C-5), 7.63 (d, ³J_{HH} = 8.8 Hz, 2H, naphth C-3), 7.25 (m, overlapping with solvent and diastereomer 2, naphth C-6), 7.19–7.11 (m, overlapping with diastereomer 2, naphth C-7 and C-8), 7.07 (m, 2H, Ph C-3), 7.05 (m, 2H, Ph C-5), 6.89 (d, ³J_{HH} = 8.7 Hz, 2H, naphth C-4), 3.12 (d, ²J_{HH} = 10.6 Hz, 2H, SCH₂), 2.57 (d, ²J_{HH} = 10.7 Hz, 2H, SCH₂), 2.29 (s, 6H, CH₃), 0.95 (s, 18H, C(CH₃)₃); ¹³C NMR (CDCl₃): δ 166.3 (Ph C-1), 159.7 (naphth C-2), 137.7 (Ph C-4), 133.5 (naphth C-9), 130.34 (Ph C-3), 130.22 (Ph C-6), 130.16 (Ph

C-5), 129.4 (naphth C-4), 127.7 (naphth C-5), 127.48 (naphth, overlapping, C-7), 125.47 (naphth, overlapping, C-8), 123.05 (naphth C-6), 119.4 (naphth C-3), 117.9 (Ph C-2), 116.0 (naphth C-1), 38.0 (overlapping, SCH₂), 34.7 (C(CH₃)₃), 28.8 (C(CH₃)₃), 20.9 (CH₃). *Diastereomer 2 (minor)*: ¹H NMR: δ 7.90 (d, ³J_{HH} = 8.8 Hz, 2H, naphth C-3), 7.82 (d, ³J_{HH} = 8.1, 2H, naphth C-5), 7.44 (d, ³J_{HH} = 8.8 Hz, 2H, naphth C-4), 7.32 (m, 2H, overlapping with diastereomer 1, naphth C-6), 7.19–7.11 (m, overlapping with diastereomer 2, naphth C-7 and C-8), 7.03 (m, 2H, Ph C-3), 6.98 (m, 2H, Ph C-5), 3.10 (d, ²J_{HH} = 10.4 Hz, 2H, SCH₂), 2.63 (d, ²J_{HH} = 10.6 Hz, 2H, SCH₂), 2.20 (s, 6H, CH₃), 1.04 (s, 18H, C(CH₃)₃). ¹³C NMR: 166.7 (Ph C-1), 159.2 (naphth C-2), 137.2 (Ph C-4), 133.6 (naphth C-9), 130.7 (Ph C-3), 130.29 (Ph C-6), 130.27 (Ph C-5), 129.5 (naphth C-4), 127.6 (naphth C-5), 127.48 (naphth, overlapping, C-7), 125.47 (naphth, overlapping C-8), 123.14 (naphth C-6), 120.5 (naphth C-3), 118.0 (Ph C-2), 115.7 (naphth C-1), 38.03 (overlapping, SCH₂), 34.9 (C(CH₃)₃), 29.1 (C(CH₃)₃), 20.7 (CH₃).

3.3. [μ-{(R)-(+)-1,1'-bi-2-naphthoxy}-μ-O-bis-(A)-{1,4-dithiabutenediyl-2,2'-bis(6-tert-butyl-4-methylphenoxy)}titanium] (2)

Following a similar procedure as reported for **1**, the crude reaction mixture was dried, redissolved in acetone and the solution was left to stand in air for 24 h. Red crystals were isolated in 80% yield, relative to (6-^tBu-4-Me-2-S-C₆H₂(OH)₂C₂H₄). ¹H NMR (CD₂Cl₂): δ 7.73 (d, 2H, naphth C-5), 7.52 (d, 2H, naphth C-3), 7.23 (t, 2H, naphth C-6), 7.11 (t, 2H, naphth C-7), 7.05 (m, 2H, Ph C-5), 7.03 (m, 2H, Ph C-5'), 6.94 (m, overlapping, 2H, Ph C-3), 6.93 (m, overlapping, 2H, Ph C-3'), 6.90 (d, 2H, naphth C-8), 6.80 (d, 2H, naphth C-4), 2.86 (ddd, ²J_{HH} = 13.7 Hz, ³J_{HH} = 2.5 Hz, ³J_{HH} = 2.5 Hz, 2H, SCH), 2.80 (ddd, ²J_{HH} = 14.1 Hz, ³J_{HH} = 2.4 Hz, ³J_{HH} = 2.4 Hz, 2H, SCH), 2.25 (s, overlapping, 6H, CH₃), 2.24 (ddd, overlapping, 2H, SCH), 2.23 (s, overlapping, 6H, CH₃), 2.11 (ddd, ²J_{HH} = 13.2 Hz, ³J_{HH} = 13.9 Hz, ³J_{HH} = 2.8 Hz, SCH), 0.94 (s, 18H, C(CH₃)₃), 0.65 (s, 18H, C(CH₃)₃). ¹³C NMR (CD₂Cl₂): δ 167.9 (Ph C-1), 167.3 (Ph C-1'), 163.9 (naphth C-2), 137.7 (Ph C-4), 137.5 (Ph C-4'), 135.1 (naphth C-9), 130.6 (Ph C-5), 130.5 (naphth C-10), 130.2 (Ph C-5'), 129.8 (Ph C-3), 129.6 (Ph C-3'), 129.4 (Ph C-6), 129.4 (Ph C-6'), 129.1 (naphth C-3), 128.3 (naphth C-5), 126.4 (naphth C-8), 125.7 (naphth C-7), 123.0 (naphth C-6), 122.4 (naphth C-4), 118.9 (Ph C-2), 117.2 (naphth C-1), 38.6 (SCH₂), 37.7 (SCH₂), 34.61 (C(CH₃)₃), 34.58 (C(CH₃)₃'), 29.5 (C(CH₃)₃), 29.2 (C(CH₃)₃'), 20.9 (CH₃), 20.8 (CH₃'). [α]_D²³ = +631.2° (c = 10.4 mg ml⁻¹, CH₂Cl₂). Anal. Calc. for C₆₈H₇₆O₇S₄Ti₂: C, 66.44; H, 6.23; S, 10.43. Found: C, 66.03; H, 6.08; S, 10.57%.

3.4. Crystallographic data for **1** and **2**

Diffraction data of [(R)-(+)-BINOLato}Ti{(C₆H₂O-^tBu-6-Me-4)₂S(CH₂)₂S}] · 2[μ-{(R)-(+)-BINOLato}-μ-O-Ti{(C₆H₂O-^tBu-6-Me-4)₂S(CH₂)₂S}] · 4(C₂H₅)₂O

Table 1
Crystal structure and structure refinement of **1** and **2**

	1 · 2 · 4Et ₂ O	3 · 2 · nH ₂ O
Formula	C ₁₉₆ H ₂₃₆ O ₂₂ S ₁₀ Ti ₅	C ₂₀₄ H ₂₂₈ O ₂₁ S ₁₂ Ti ₆
Formula weight (g mol ⁻¹)	3503.95	3687.98
Crystal size (mm)	0.19 × 0.18 × 0.04	0.4 × 0.3 × 0.2
Color	Red	Red
Crystal system	Monoclinic	Triclinic
Space group	<i>P</i> 2 ₁	<i>P</i> 1
Unit cell dimensions		
<i>a</i> (Å)	14.6512(14)	14.766(4)
<i>b</i> (Å)	33.597(3)	21.822(6)
<i>c</i> (Å)	21.137(2)	21.862(9)
α (°)	90	114.698(9)
β (°)	106.946(3)	105.500(11)
γ (°)	90	99.664(9)
<i>V</i> (Å ³)	9952.6(16)	5844(3)
<i>Z</i>	2	1
<i>D</i> _{calc.} (g cm ⁻³)	1.169	1.048
Temperature (K)	110(2)	153(2)
Number of collected reflections	92119	81104
Number of independent reflections [<i>R</i> _{int}]	24437 [0.1740]	39846 [0.1039]
Parameters	2024	2236
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	0.0776, 0.1553	0.0774, 0.1415
<i>R</i> indices (all data)	0.1569, 0.1862	0.1569, 0.1642
Goodness-of-fit on <i>F</i> ²	0.974	0.893
Flack parameter	-0.04(3)	0.04(2)

(**1** · 2 · 4 Et₂O) as well as of 3[μ -{(R)-(+)-BINOLato}- μ -O-{Ti[(C₆H₂O-*t*Bu-6-Me-4)₂S(CH₂)₂S]}₂]} · nH₂O were obtained with a Bruker AXS SMART CCD diffractometer with graphite monochromated Mo K α radiation using ϕ and ω scans. The data reductions as well as absorption corrections were carried out using the SMART program [16a]. The structures were solved by direct methods and Fourier methods using the programs SHELXS-86 [16b] and SHELXL-96 [16c]. Anisotropic thermal parameters were refined for nearly all of the non-hydrogen atoms. Only the ether molecules in the crystal containing **1** as well as three other non-hydrogen atoms in this structure were refined with isotropic thermal parameters. All hydrogen atoms were included into idealized positions. Due to the poor quality of the crystal that contains the compound **1**, only data up to a θ value of 22° could be collected. The second crystal structure contains three independent molecules of **2** and also a large void (1425 Å³ according to PLATON [16d]). ¹H NMR spectroscopy showed that crystals of **2** incorporate a large amount of H₂O. Due to the unresolvable disorder, the water molecules in the crystal were squeezed out using PLATON [17]. The results of the crystal structure determinations are given in Table 1.

4. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Center; Publication Nos. 292653 (**1**) and 292654 (**2**).

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