Molecular structure of 2,2'-thiobis(4-methyl-6-tert-butylphenoxy) titanium diisopropoxy. Influence of titanium–sulfur interaction on coordination geometry

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Abstract

The molecular structure of 2,2'-thiobis(4-methyl-6-tert-butylphenoxy) titanium diisopropoxy (**1a**) has been determined. The molecule exists as a dimer, in which the 1,3-dioxadititanacycle is supported by two bridging ^iPrO ligands. The coordination environment about each Ti center is best described as a distorted octahedron, where the S atom and one ^iPrO ligand occupy the axial positions, whilst two terminal phenolate and two bridging ^iPrO ligands occupy the equatorial sites. The eight-membered dioxatitanacycle adopts a symmetric-*syn* boat conformation, which allows for a significant sulfur–titanium interaction (S–Ti distance 2.724(2) Å). A comparison between these structural features and those reported for the monomeric tetrahedral complexes **2b** and **2d**, where the sulfur atom is replaced by a methylene bridge in the bisphenoxy ligand, highlights the influence of the S–Ti interaction on coordination geometry. The structural features suggested for **1a** to account for the higher catalytic activity of **1a**/MAO in polymerization of α-olefins as compared with **2a**/MAO are clearly demonstrated.
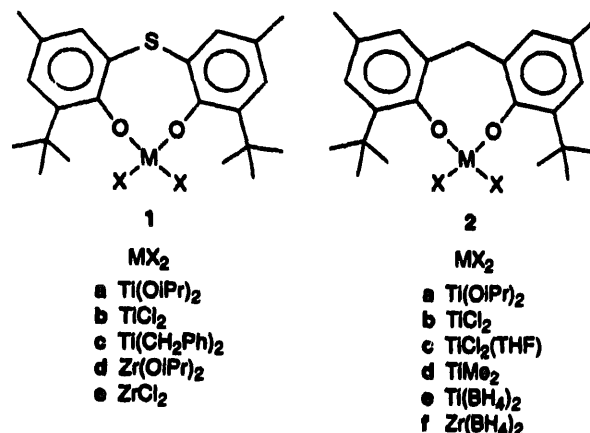
Keywords: Titanium; 2,2'-Thiobisphenoxy ligand; Sulfur; Sulfide; X-ray structure; Ti–S interaction

1. Introduction

Phenolate complexes of Group IV transition metals in combination with MAO have been reported recently to polymerize olefins and diolefins [1].

Of particular interest are the catalysts prepared from 2,2'-thiobis(4-methyl-6-tert-butylphenoxy)MX$_2$(**1a–e**) and 2,2'-methylenebis(4-methyl-6-tert-butyl phenoxy)-MX$_2$(**2a,b**) (Scheme 1). These catalysts have been used for the polymerization of ethylene [1a,c–e], propylene [1a,c], styrene [1b,c] and some dienes [1c–e], and also for the alternating copolymerization of ethylene and styrene [1b,c]. The catalysts prepared from **1a,b** have been found to be more active than those prepared from **2a,b** in the polymerization of styrene [1b,c], ethylene [1e] and 1,3-dienes [2]. It has been speculated that this difference of activity may be due to an increased ligand

flexibility and to effects of possible π-donation from sulfur to titanium in **1a,b** [1c,e]. Indeed, in some compounds of phosphorus [3] and silicon [4] with chelating 2,2'-thiobisphenoxy ligands a significant P–S or Si–S

Scheme 1.

1
MX$_2$
a Ti(OiPr)$_2$
b TiCl$_2$
c Ti(CH$_2$Ph)$_2$
d Zr(OiPr)$_2$
e ZrCl$_2$

2
MX$_2$
a Ti(OiPr)$_2$
b TiCl$_2$
c TiCl$_2$(THF)
d TiMe$_2$
e Ti(BH$_4$)$_2$
f Zr(BH$_4$)$_2$
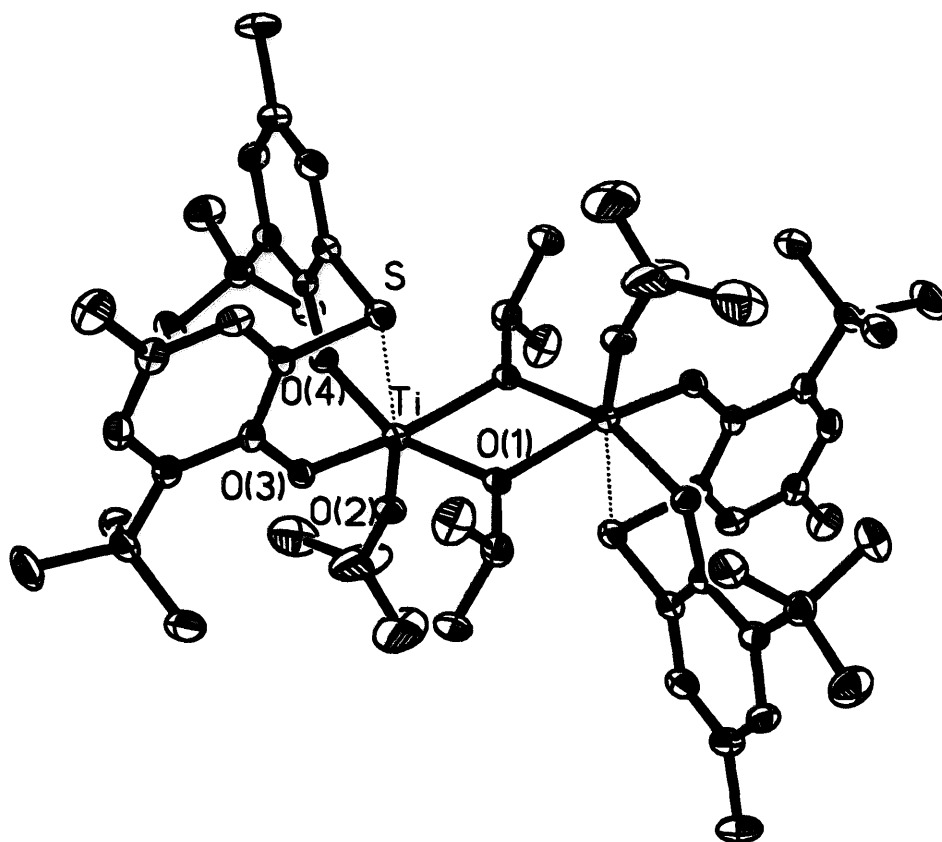
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Fig. 1. Structure of the binuclear complex 1a. Selected bond lengths (Å) and angles (°): Ti–O1 2.014(3), Ti–O1# 2.029(3), Ti–O2 1.767(3), Ti–O3 1.878(3), Ti–O4 1.899(3), Ti–S 2.724(2); O2–Ti–O3 98.4(2), O2–Ti–O4 99.0(2), O3–Ti–O4 92.5(2), O2–Ti–O1 101.2(2), O3–Ti–O1 95.47(14), O4–Ti–O1 156.95(14), O2–Ti–O1# 102.9(2), O3–Ti–O1# 157.43(14), O4–Ti–O1# 91.39(14), O1–Ti–O1# 73.30(14), O2–Ti–S 171.97(12), O3–Ti–S 76.34(11), O4–Ti–S 75.46(11), O1–Ti–S 85.48(10), Ti–O1–Ti# 106.70(14). (#, Equivalent atoms generated by the symmetry transformation −x + 1/2, −y + 1/2, −z.)
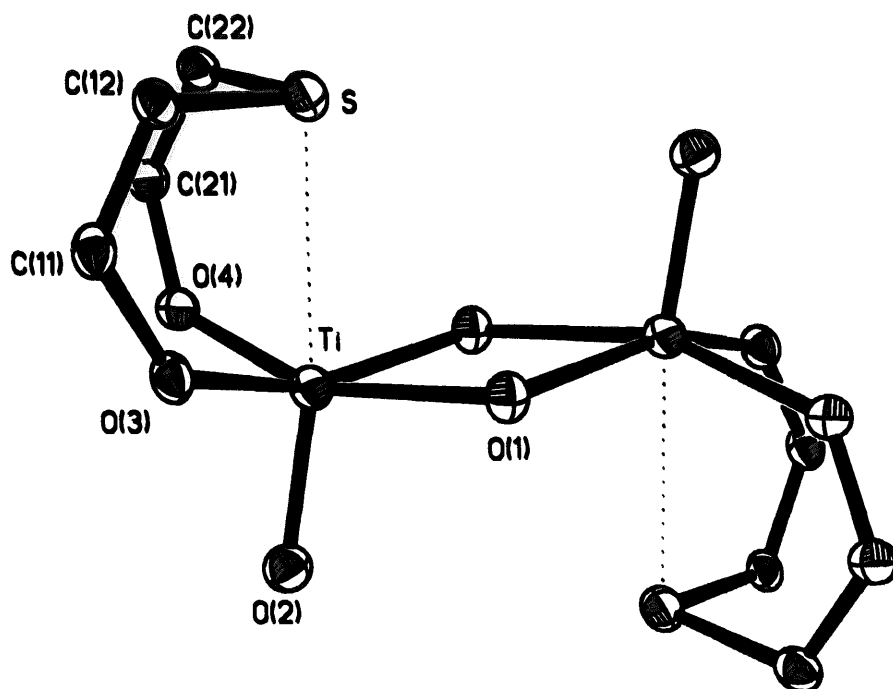

Fig. 2. The immediate coordination sphere of Ti atoms in complex 1a.

interaction has been found. Although the molecular structures of **2b** [5a], **2c** [5c], **2d** [5a], **2e** [5b] and **2f** [5b] have been determined by X-ray diffraction, no structural data are available on the thio analogues **1a–e**. Our interest in the polymerization of dienes with catalysts prepared from **1a–e** prompted us to investigate the molecular structure of **1a**. The distinctive structural features suggested for **1a,b** to account for the higher catalytic activity of **1a,b**/MAO as compared with **2a,b**/MAO in polymerization reactions are clearly demonstrated in this communication.

2. Experimental, results and discussion

Complex **1a** was prepared following a modification of a literature procedure [1a,6]. Red crystals of **1a** were obtained from a toluene/hexane solution at room temperature.

Fig. 1 shows the binuclear 2,2'-thiobis(4-methyl-6-tert-butylphenoxy) titanium diisopropoxy complex as determined from the crystallographic investigation. Fig. 2 shows the immediate coordination sphere of the Ti atoms, displaying two edge-fused octahedra.

The most distinctive feature of **1a** is the Ti–S distance of 2.724(2) Å, ca. 0.8 Å shorter than the sum of the Van der Waals radii of the two atoms [7] but substantially longer than Ti–S single bonds (typically 2.3–2.4 Å) [8]. The geometry of the Ti–S interaction is characterized by an angle of 4° between the normal to the plane defined by S, C22, C12 and the Ti–S direction (see Fig. 2). The value of this angle is somewhat small but compatible with one of the sulfur lone pairs interacting with the electrophilic Ti atom. Similar interactions with divalent sulfur have been reported for various atomic species [9], but so far not with Ti. Its attractive nature clearly results from the participation of the S atom in the distorted octahedral coordination geometry of Ti [10]. The S atom and one ^{i}PrO ligand occupy the axial positions, whilst two terminal phenolate and two bridging ^{i}PrO ligands occupy the equatorial sites. All the O–Ti–O and O–Ti–S bond angles are reasonably consistent with this description. A substantial distortion from octahedral coordination in **1a** relates to the bridging oxygen atoms (O1–Ti–O1* = 73.3(1)°) and is dictated by the geometry of the 1,3-dioxatitanacycle. Accordingly, the Ti–O1 and Ti–O1* bond distances are substantially elongated. Indeed, all these features and the Ti(1)–Ti(#1) distance of 3.243(2) Å correspond closely to the geometries observed in other d^0–d^0 dinuclear complexes containing a Ti–O–Ti–O core [5e,10,11].

However, if only the alkoxy groups are considered and the S–Ti interaction is disregarded, the coordination can be described as distorted square-pyramidal with the Ti atom displaced by 0.346 Å from the plane defined by
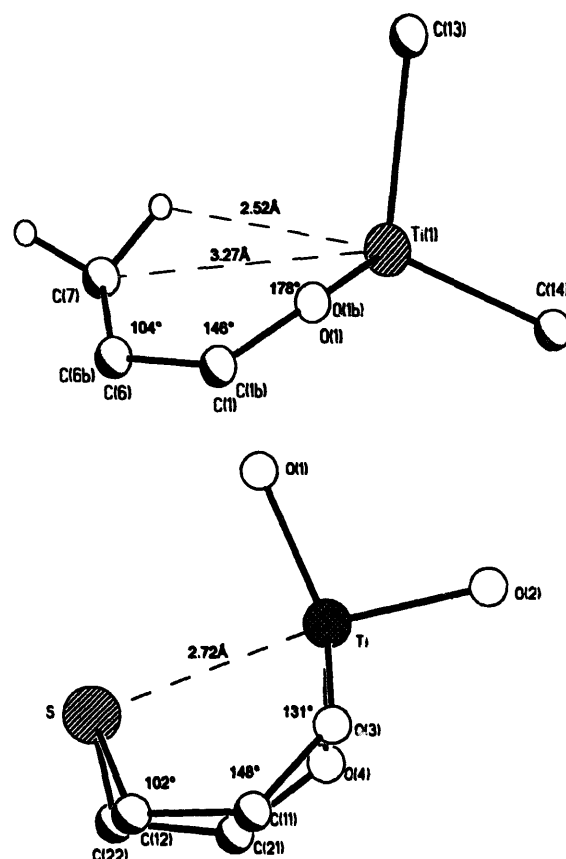

Fig. 3. A comparison of the eight-membered ring geometry in **2d** (from Ref. [5b]) (top) and **1a** (bottom), evidencing the dihedral angles between least-squares planes and relevant interatomic contacts.

O3, O4, O1 and O1' in the direction of the apical O2 atom (see Fig. 2). Consistent with this description the bond to the apical O2 atom is the shortest Ti–O bond.

A comparison with the dimeric complex [(Me$_2$-BINO)Ti(O-^{i}Pr)$_2$]$_2$ [5e] (H$_2$Me$_2$BINO = 3,3'-dimethyl-1,1'-bi-2-naphthol), which bears similar ligands, is of interest. The coordination environment about each Ti center in this compound is a highly distorted trigonal bipyramid, with a bridging naphtholate ligand and one ^{i}PrO ligand in the axial positions, whilst one ^{i}PrO, a terminal naphtholate and a bridging naphtholate ligand occupy the remaining equatorial sites. A trigonal-bipyramidal arrangement has also been recently observed for **2c** [5c]. Thus, it seems that in the case of **1a** the S atom has a major role in determining the octahedral (or the square-pyramidal) coordination.

An additional structural feature evidencing the attractive nature of the Ti–S interaction is the symmetric-*syn* boat conformation of the eight-membered dioxatitanacycle of **1a**, which differs from that adopted by **2b** and **2d** [5a]. As shown in Fig. 3, the dihedral angle between the planes defined by Ti, O3, O4 and O3, O4, C21, C11 in **1a** is 131°, whilst the corresponding angle in **2d** has a

value of 178°. Accordingly, the S–Ti distance in **1a** (2.724(2) Å) is considerably shorter than the distance, close to 3.30 Å, between the carbon of the methylene bridge and the titanium atom in **2b** and **2d**. The Ti–O–C_{Ar} angles (average value 132° for **1a** and 145° for **2b,d**) are also different [12], which reflects the lower Ti–O_{Ar} bond order as well as the larger Ti–O_{Ar} bond distances in **1a** as compared with **2b** and **2d**.

Although the Ti–S interaction is probably weak, it is likely to be of importance in stabilizing the active cationic species [13,14], facilitating its formation from **1a,b** and MAO and making the coordination of the counterion less tight [15]. These effects would account for the enhanced overall activity of the catalysts prepared from **1a,b**. Further work aimed at gaining more insight into the nature of the active species is in progress.

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[6] *Experimental procedure* (**1a**). The reaction was performed under argon atmosphere using Schlenk techniques. Freshly distilled Ti(O-$^iPr)_4$ (0.68 ml, 2.29 mmol) was added to a stirred solution of 2,2'-thiobis(4-methyl-6-tert-buthylphenol) (0.820 g, 2.29 mmol) in 20 ml of dry toluene at ambient temperature. The solution became immediately red, and turned to a red suspension in a few minutes. ^iPrOH which formed was removed by azeotropical distillation. After evaporation of the solvent in vacuo, the orange–red solid was washed with hexane and dried

(89% yield). Anal. Found: C, 64.42; H, 8.19. $C_{28}H_{42}O_4STi$. Calc.: C, 64.35; H, 8.10%. ^1H NMR (200 MHz, $CDCl_3$, 298 K): δ 1.31 (d, 12H, J = 6 Hz, CH(C$H_3)_2$), 1.32 (s, 18H, C(CH$_3)_3$), 2.20 (s, 6H, CH$_3$Ar), 4.80 (m, 2H, J = 6 Hz, CH(CH$_3)_2$), 6.92 (d, 2H, J = 2 Hz, H$_{Ar}$), 7.12 (d, 2H, J = 2 Hz, H$_{Ar}$). (Additional signals of low intensity were also detected and not attributed. The ^1H NMR spectrum of **1a** was recorded in $CDCl_3$ because of the practical insolubility of **1a** in other solvents.)

Crystals of **1a** suitable for X-ray analysis were obtained by dissolving the solid (20 mg) in toluene (10 ml) at 89°C. The solution was allowed to cool slowly to room temperature, and a layer of heptane (1 ml) was added. After two weeks, a few red crystals of **1a** formed.

X-ray diffraction data of a crystal of size 0.25×0.20×0.10 mm^3, sealed in a thin-walled glass capillary under argon atmosphere, were collected on a SIEMENS P4 diffractometer with graphite-monochromated Cu K α radiation (λ = 1.5418 Å). Cell constants were obtained by least-squares refinement on the 2θ value of 24 reflections with 2θ > 40°. The θ/2θ scan technique was used to collect two octants of intensity data with 3.33° < 2θ < 56.75° for 3976 independent reflections (R_{int} = 0.0418). Three standard reflections were monitored every 97 reflections to check crystal orientation and stability.

Data were corrected for Lorentz and polarization effects and an empirical absorption correction based on ψ scans was applied. The structure was solved by direct methods using SIR92 [16] and refined by full-matrix least-squares on F^2 using SHELXL93 [17]. Non-hydrogen atoms were refined anisotropically while hydrogen atoms, included at calculated positions, were refined in the riding mode with group temperature factors.

The ^iPr group attached to the non-bridging oxygen atoms (O2) appears to be disordered. For the atoms of this ligand only one set of geometrical parameters is given, because no more detailed model for describing the disordering mode was found. Thermal parameters of the atoms of this group are consequently large.

Crystal data of **1a**. $C_{28}H_{42}O_4STi$, M = 1045.15, monoclinic, space group $C2/c$, a = 17.746(2) Å, b = 20.429(2) Å, c = 16.610(3) Å, β = 99.930(2)°, V = 5931.5(14) Å^3, D_c = 1.170 mg m^{-3}, μ = 3.322 mm^{-1}, F(000) = 2240, index ranges −1 ≤ h ≤ 19, −1 ≤ k ≤ 22, −18 ≤ l ≤ 17, 325 parameters, S = 1.044, R_1 = 0.058 for 2375 data with I > 2σ(I), wR_2 = 0.1377, (for all 3970 data), extinction coefficient 0.000048(13), largest difference peak and hole 0.293 and −0.260 eÅ^{-3}.

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