



# DFT analysis of titanium complexes with oxygen-containing bidentate ligands

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## Abstract

Strength of the Ti–O co-ordinate bond in several titanium complexes with bidentate ligands has been investigated by means of DFT. Mutual interaction of particular donors and their influence on Lewis acidity of the central atom have also been studied. The energy of ligand binding ranges from –19 to –454 kJ/mol, depending on the kind of donors. Calculations confirm that a strong donor, alkoxide anion, co-ordinatively saturates the titanium and makes binding of new ligands less exoenergetic. On the contrary, two oxygen atoms of similar donor number do not have much influence on each other.

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## 1. Introduction

Bidentate oxygen-containing ligands have become the attractive components of heterogeneous catalysts of  $\alpha$ -olefin polymerisation. This class of compounds includes, among others, diethers, esters of dicarboxylic acids and certain derivatives of tetrahydrofuran. Historically, one of the first bidentate Lewis base commercially applied as an external donor was dibutyl phthalate [1], whose role and mechanism of action in the catalytic system have been unravelled only recently by means of computer molecular modelling [2]. Modern catalytic systems contain greater selection of more sophisticated donors that enhance their activity and/or stereoselectivity. The interaction of donors, such as diethers,

with the support have also been studied theoretically [3].

Bidentate ligands containing two different functional groups are of special interest. It is obvious that the energy of co-ordinate bonds between the transition metal atom and oxygen atoms might be significantly different. This phenomenon might have a pronounced effect on the properties of a catalyst. In the polymerisation medium, the bidentate ligand competes for the co-ordination to the transition metal atom with the other components, such as olefin and organoaluminium compound. It is obvious that the availability of two varied functional groups containing oxygen atoms of different donor number in the molecule of particular Lewis base provides better control over the properties of a catalyst. Therefore, the knowledge of the energy of these bond seems to be important.

This paper reports the results of study of the strength of co-ordinate bonds in the complexes of titanium(IV) with the following bidentate ligands:

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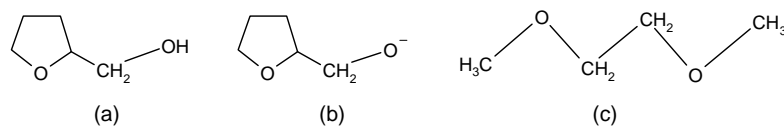


Fig. 1. Three ligands studied: (a) tetrahydrofurfuroxol; (b) tetrahydrofurfuroxo anion; (c) dimethyl ether of ethylene glycol.

tetrahydrofurfuroxol (THFFOH), tetrahydrofurfuroxo anion (THFFO), dimethyl ether of ethylene glycol (Fig. 1) and a monodentate ligand — tetrahydrofuran (THF). All the bidentate ligands have a common structural feature: two oxygen atoms separated by two aliphatic or one aliphatic and one alicyclic carbon atoms. However, the donor numbers of particular oxygen atoms differ to some extent, since these atoms belong to hydroxyl, alkoxy, aliphatic and heterocyclic ether groups, respectively. The mutual interaction of ligands and the modifications of the acidity of the central atom caused by the presence of different ligands is also discussed.

In the experimental part of this study, we have focused on five THFFO-based complexes (I–V) synthesised and characterised by Sobota et al. [4] as well as two monodentate ligands: dimethyl ether of ethylene glycol (VI) and THF (VII) (Table 1). The polymerisation tests with carried out by us indicate that they form the catalysts whose activities range from 33 to 312 kg PE/(gTi·h). The catalysts were prepared by milling one of these compounds in hexane slurry with the support [MgCl<sub>2</sub>(THF)<sub>2</sub>]. AlEt<sub>3</sub> and its derivatives were applied as co-catalysts (Mg:Ti = 10; [Ti] = 0.01 mmol/dm<sup>3</sup>; [Al] = 5 mmol/dm<sup>3</sup>).

Table 1  
Titanium complexes containing THFFO ligands and their activity in ethylene polymerisation

Complex	Activity (kg PE/(gTi·h))
I [Ti <sub>2</sub> (μ-Cl) <sub>2</sub> Cl <sub>4</sub> {η <sup>2</sup> -OCH <sub>2</sub> CH(CH <sub>2</sub> ) <sub>3</sub> O <sub>2</sub> } <sub>2</sub> ]	312.1
II [TiCl <sub>3</sub> (THF){η <sup>2</sup> -HOCH <sub>2</sub> CH(CH <sub>2</sub> ) <sub>3</sub> O <sub>2</sub> } <sub>2</sub> ]	160.3
III [TiCl <sub>2</sub> {η <sup>2</sup> -OCH <sub>2</sub> CH(CH <sub>2</sub> ) <sub>3</sub> O <sub>2</sub> } <sub>2</sub> ]	224.5
IV [TiCl <sub>3</sub> {(CH <sub>2</sub> ) <sub>4</sub> O}{η <sup>2</sup> -OCH <sub>2</sub> CH(CH <sub>2</sub> ) <sub>3</sub> O <sub>2</sub> } <sub>2</sub> ]	246.3
V [TiCl <sub>3</sub> (TMEN){η <sup>1</sup> -OCH <sub>2</sub> CH(CH <sub>2</sub> ) <sub>3</sub> O <sub>2</sub> } <sub>2</sub> ]	149.5
VI [TiCl <sub>4</sub> {η <sup>2</sup> -CH <sub>3</sub> O(CH <sub>2</sub> ) <sub>2</sub> OCH <sub>3</sub> }]	32.8
VII <sup>a</sup> [TiCl <sub>4</sub> {(CH <sub>2</sub> ) <sub>4</sub> O}] <sub>2</sub>	212.0

TMEN: *N,N'*-tetramethylethylenediamine.

<sup>a</sup> Polymerisation results taken from [5].

## 2. Computational details

Stationary points on the potential energy surface (PES) were calculated and characterised using the Gaussian 98 molecular modelling package [6]. The hybrid, three-parameter gradient-corrected density functional by Becke, Lee, Yang and Parr (B3LYP) [7,8] and the LANL2DZ basis set [9–12], which includes the double-zeta basis set and effective core potential replacing chemically inert core electrons for the elements of  $Z > 10$ .

The computational procedure applied both for the ligands and the complexes is shown schematically in Fig. 2. The dihedral angle  $\alpha$ , formed by the –O–C–C–O– bonds was increased stepwise every 10° by rotation around the C–C bond (which is almost perpendicular to the plane of drawing in Fig. 2). In each step, the full optimisation of the structure was performed (relaxed scan) and the energy of the system was calculated. The full range of angles from –180 to +180° was covered by the scans. As a result of rotation around the C–C bond, one of the Ti–O co-ordinate bonds (the weaker one) was broken. The

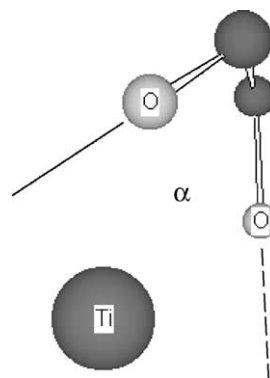


Fig. 2. Forced rotation around the C–C bond breaks one of the Ti–O co-ordinate bonds. For the sake of clarity, most of the ligand atoms are hidden.

energy required to increase the value of the  $\alpha$  dihedral angle corresponds to the energy of that bond.

### 3. Structure of ligands

The results of PES scanning as a function of the  $-\text{O}-\text{C}-\text{C}-\text{O}-$  dihedral angle ( $\alpha$ ) for the THFFO and dimethyl ether of ethylene glycol ligands, shown in Fig. 3, give some information concerning the structure of these ligands. Firstly, both profiles show distinct maxima for the  $\alpha$  values approximating  $0^\circ$ , which is related to repulsion between two oxygen atoms. Secondly, the minima present for the *anti*-conformation ( $\alpha = 180^\circ$ ) correspond to the maximum distance between the oxygen atoms. For the dimethyl ether of ethylene glycol (Fig. 3a), these are the global minima, whereas the THFFO ligand shows a global minimum

for  $\alpha = 71^\circ$  (Fig. 3b). Such a conformation places the oxygen atom belonging to the alkoxy group over the heterocyclic ring. Finally, the PES profile for dimethyl ether of ethylene glycol is symmetrical.

### 4. Complexes with $\text{TiCl}_4$

#### 4.1. Dimethyl ether of ethylene glycol

Initially, the PES profile for the complex VI was obtained by two different methods. In the first method, the  $\alpha$  dihedral angle was modified and the remaining distances and angles were frozen (rigid scan). The second method produced the so-called relaxed scan, in which all the variables were optimised. Both profiles, shown in Fig. 4, are similar to the profile of the corresponding ligand. The energetic maximum appears for

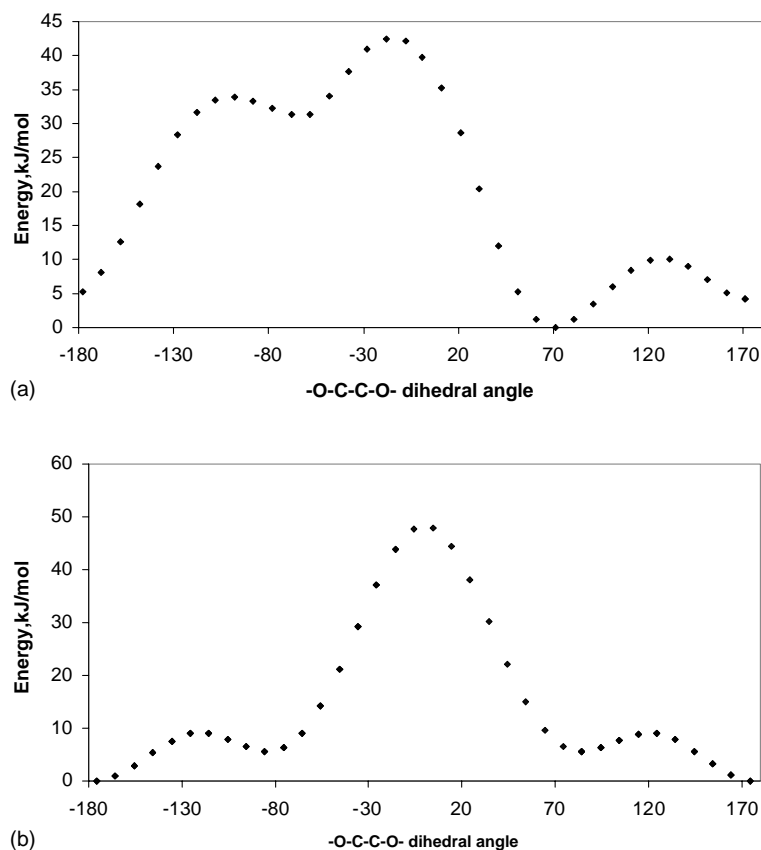


Fig. 3. PES profiles for the ligands: (a) THFFO; (b) dimethyl ether of ethylene glycol.

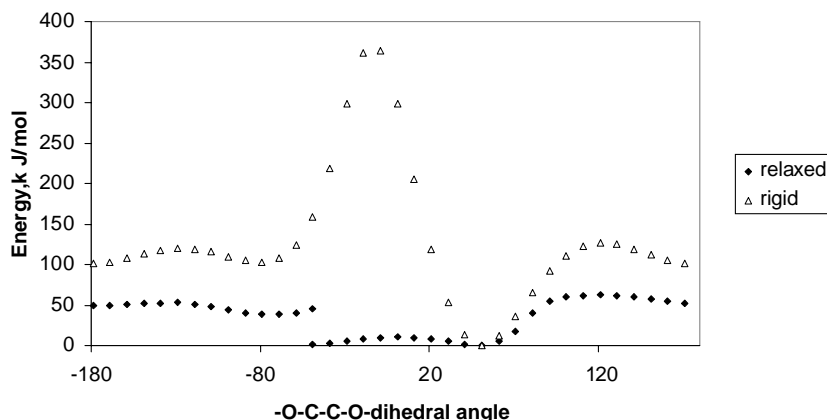


Fig. 4. Relaxed and rigid PES scans for complex VI.

the *syn*-conformation. A huge difference in the maximum value of energy is caused by the method applied — the rigid scan leads to steric hindrance and strong repulsion between the methylene hydrogen atoms and the titanium atom, whose position is not optimised. This leads to the increase in the total electronic energy of the system.

The PES profile for the relaxed scan has a discontinuity at  $\alpha = -49^\circ$ , which is caused by the geometry re-optimisation in each step and different starting geometry around this point. In its left-hand side, the optimisation starts from the geometry of the  $[\text{TiCl}_4\{\eta^1\text{-CH}_3\text{O}(\text{CH}_2)_2\text{OCH}_3\}]$  species, in which dimethyl ether of ethylene glycol is a monodentate ligand.

#### 4.2. THFFO and THFFOH ligands

DFT calculations on complex I would be rather time-consuming since the complex contains 40 atoms. In order to decrease computational power requirements, the model of this compound was reduced by us to obtain hypothetical species  $[\text{TiCl}_4\{\eta^2\text{-OCH}_2\text{CH}(\text{CH}_2)_3\text{O}\}]^-$  (I'). This simplification did not impact the results of structure optimisation. The  $\alpha$  dihedral angle of  $36.6^\circ$  is in good agreement with the value of  $35.1^\circ$  taken from [4].

The THFFO ligand, unlike dimethyl ether of ethylene glycol, contains two oxygen atoms of different reactivity and different donor number. Therefore, this

ligand forms two Ti–O bonds of different strength. The oxygen atom belonging to the heterocyclic ring forms much weaker bond with the titanium atom, comparing to the other oxygen atom. According to the PES scanning profile shown in Fig. 5, the energy required to increase the  $\alpha$  dihedral angle from  $36.6^\circ$  to  $60^\circ$  and break the weaker bond is 19 kJ/mol.

The PES profile has a global minimum for  $\alpha = 180^\circ$  which corresponds to the structure  $[\text{TiCl}_4\{\eta^1\text{-OCH}_2\text{CH}(\text{CH}_2)_3\text{O}\}]^-$  (I''), where THFFO is a monodentate ligand linked through the alkoxy oxygen atom with the transition metal atom. This phenomenon is crucial for the catalytic behaviour of metal alkoxides since the open co-ordination site at the metal atom is potentially capable of binding other ligands [4], including ethylene molecules. Additionally, the energy difference between the local and global minima in Fig. 5 is only 10 kJ/mol.

In order to obtain more information concerning the energy of bonds between titanium and oxygen atoms that belong to different functional groups, the PES profile for the species  $[\text{TiCl}_4\{\eta^2\text{-HOCH}_2\text{CH}(\text{CH}_2)_3\text{O}\}_2]$  (II') was computed. The curve shown in Fig. 6 differs from the one presented in Fig. 5. Increased  $\alpha$  leads to the removal of a hydroxyl group from the titanium co-ordination sphere, which requires 67 kJ/mol. Therefore, unlike the previous case, the oxygen atom belonging to the heterocyclic ring still remains bound to the titanium atom.

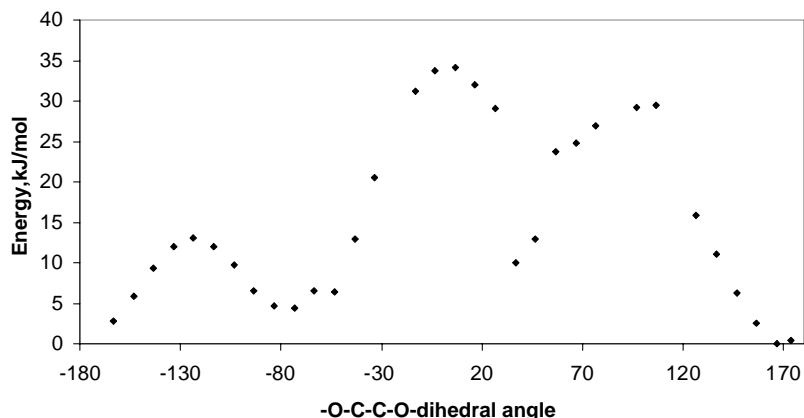


Fig. 5. PES scan for species I'.

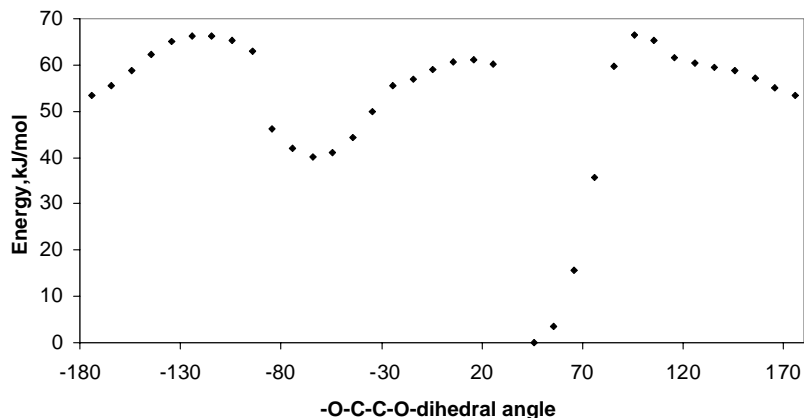


Fig. 6. PES scan for species II'.

#### 4.3. Mutual interaction of ligands

Discussion of the complexes with bidentate ligands must include the mutual interaction of both donor

atoms and the modifications of Lewis acidity of the metal atom caused by these atoms. It is best seen when one compares the energies required to break particular co-ordinate bonds with the total energy of formation

Table 2

Energy of the Ti–O bond formation and breaking for the oxygen atoms belonging to different functional groups in mono- and multidentate ligands

Species	Formation energy (kJ/mol)	Energy of breaking the Ti–O co-ordinate bond (kJ/mol)		
		Hydroxyl	Diether	Heterocyclic
I'	–473	–	–	+19
II'	–114	+67	–	–
VI	–108	–	+63	–
VII	–176	–	–	+94

of complex from the isolated substrates — titanium tetrachloride and ligands in their optimal conformation (Table 2).

In the case of the complexes of multidentate ligands containing two chemically identical oxygen atoms (such as dimethyl ether of ethylene glycol) or two identical monodentate ligands (such as tetrahydrofuran), the energy required to break one of the bond equals approximately half of the formation energy. On the other hand, the energy is not equally distributed between the two different co-ordinate bonds. Table 2 indicates that for the species I', the energy required to break the weaker bond is only a small fraction of the total energy of complexation. It may be concluded that the alkoxide anion is such a strong electron donor that it co-ordinatively saturates the titanium atom and lowers its Lewis acidity.

## 5. Conclusions

We have demonstrated the differences between the Ti–O co-ordinate bonds in the complexes of titanium tetrachloride with oxygen-containing bidentate ligands. Huge differences in distribution of the complex formation energy exist if titanium forms two co-ordinate bonds with oxygen atoms belonging to different functional groups. In such a situation, one of these bonds can break easily, which leads to the formation of complexes with monodentate dangling ligands. It is believed that such behaviour is vital in the process of olefin polymerisation. There is experimental evidence that the catalysts prepared from the complexes of titanium with bidentate ligands containing different functional groups reach the activity of those with monodentate ones. On the contrary, catalysts obtained from the complexes of titanium with bidentate ligands containing chemically identical donors show moderate activity.

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