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A density functional theory study of bridging and terminal oxotitanium(IV) oligomeric and polymeric linear titanoxanes

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Abstract. This work deals with theoretical investigations on the oxygen–transition metal bond in systems containing linear chains of Ti–O units. From an experimental point of view, in the recent past a number of systems containing linearly arranged Ti–O units were synthesized, in which the Ti atom is complexed with Schiff bases such as acacen and salen. The theoretical study presented here has been carried out applying the density functional theory to model compounds of these systems, in order to shed light on the interactions between the transition metal and oxygen. Calculations have been performed on Ti–O oligomers (dimers, trimers and tetramers) by means of density functional theory at the gradient-corrected level of theory, optimizing the molecular geometries. Calculations have also been performed on linear polymers of the same systems, applying periodic boundary conditions, in order to compare the results with those of oligomeric analogues.

Key words: Titanoxanes – Extended systems – Density functional calculations – Electronic structure – Band structure

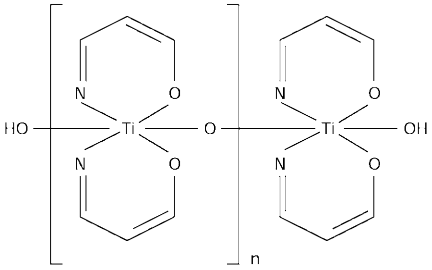
1 Introduction

In the recent past, much attention has been attracted by titanoxanes [1], because of their potential use in the field of material chemistry and also to the bridging role of this class of compounds between molecular and solid-state chemistry [2]. In particular, recent investigations have been focused the chemistry of Ti–O functionality, which may occur as bridging Ti–O–Ti or terminal Ti=O. The chemistry of the interconversion of these functionalities has been investigated from both experimental and theoretical points of view [3]. In these studies, it has been found that the controlled ionization of the linear Cl–Ti–O–Ti–Cl skeleton allows the generation of the $(Cl–Ti–O{=}Ti)^+$ dimer, which is nonsymmetrical as a consequence of extended Cl–Ti–O π interactions. The Ti=O unit thus formed is a building block for a variety of extended titanoxane structures.

The main aim of this work is to shed light, by means of quantum mechanical calculations, on the properties of the oxygen–transition metal bond in systems containing linear chains of Ti–O units. The starting point for the theoretical calculations consists of the available experimental data for linearly arranged Ti–O containing systems. The Ti–O units may be constrained to arrange in a linear fashion using tetradentate Schiff base complexes, such as acacen and salen [4]. In such a way, dimers, trimers and tetramers of Ti–O units were obtained and structurally characterized [3].

2 Models

In order to make feasible theoretical calculations, a modeling of the Schiff base has been done. Particularly, only acacen-type ligands were taken into account, and they were simulated by two symmetrical –O–CH=CH–CH=NH– planar ligands. Calculations were carried out on dimers, trimers and tetramers of Ti–O units, terminated with an –OH group, which correspond to the structure depicted in Scheme 1 with $n = 1, 2, 3$.



Calculations were also performed on models of doubly ionized solvated systems, substituting the two OH^-

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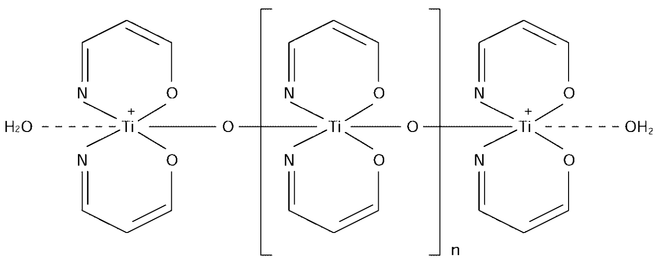
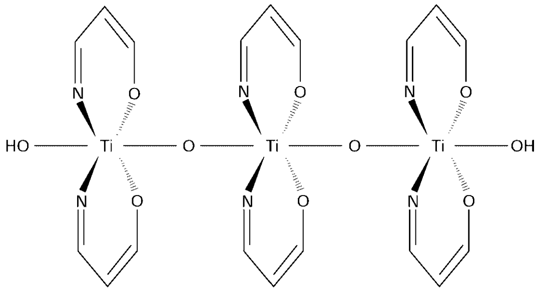
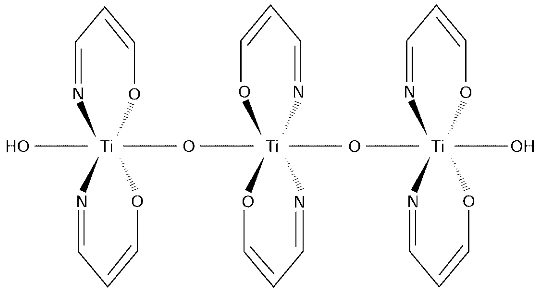
terminal groups with two water molecules, as shown in Scheme 2 (n=0, 1, 2).



This allows comparisons of the theoretical optimized geometries with the experimental structures. For all the systems a geometry optimization with symmetry constraints was carried out, analyzing in detail the geometry of the linear Ti–O skeleton. For such systems, two conformations (syn and anti) are possible, depending on the relative orientation of adjacent aromatic rings (Scheme 3).



syn



anti

Although the X-ray structures show that the anti conformation is preferred, calculations were carried out on both structures in order to check the energy difference between the two arrangements. Calculations on both the syn and the anti conformations were also carried out on polymers; in both cases the unit cell contains two titanium atoms.

3 Methods and computational details

Density functional theory (DFT) was used in all the calculations on both the oligomers and the polymers. The exchange and correlation functionals were evaluated at the gradient-corrected level of theory; the approximations due to Becke [5] and Perdew [6] were used. The effectiveness of such approximations for the exchange and correlation functionals in dealing with transition-metal complexes, particularly with transition metal-oxides, has been proved by several works in the course of the last few years [7, 8]. The basis set was chosen by adopting a compromise between accuracy and computational effort. We used two valence functions (double-ζ) for each nonmetallic atom and three valence functions and a polarization function (triple-ζ–p) for the transition-metal atoms. The use of this kind of basis set has been demonstrated to be successful in studying the properties of several transition-metal complexes, concerning especially geometry optimizations, as shown, for instance, in some recent works by our group [9, 10]. We also checked the effect of polarization functions added to the oxygen atoms belonging to the main chain, and found optimized molecular geometries substantially identical to those obtained using the nonpolarized basis set. Localized Slater-type atomic functions were used in discrete systems, whereas both Slater-type and "numerical" atomic orbitals [11] were used for extended systems. All the calculations were performed on the singlet ground state at closed-shell level.

Geometry optimizations were carried out for all the discrete systems considered, both with and without the constraint of a symmetrical distribution of Ti–O distances with respect to the chain center. The aromatic rings bearing the Ti atoms were constrained in a planar geometry. Moreover, molecular orbital analysis was also performed in order to compare the ordering of energy levels corresponding to oxygen–metal interactions with the extended system crystal orbitals.

Calculations on the polymers were performed on fixed structures using the geometric parameters taken from the optimized tetramer central unit; however, partial geometry optimizations were performed on the oxygen–metal distances along the polymer skeleton. The optimizations regarded both systems with uniform oxygen–metal distances and systems with an alternate arrangement of two different oxygen–metal distances, in order to verify the occurrence of a Peierls distortion.

Energy level results obtained in the reciprocal space (energy bands) were brought back into real space by means of density of state (DOS) averaging. Bond localization was also done by projecting the total DOS on atomic orbitals (PDOS) and evaluating crystal orbital overlap populations (COOP), in order to distinguish bonding from antibonding interactions.

All the calculations on the discrete molecules were performed using the ADF program package [12]; the calculations on the polymers were done using the BAND program package [13]. The homogeneity of the DFT approach in these two packages made feasible comparisons between the results for discrete and extended systems.

4 Results and discussion

Considerations about the nature of titanium–oxygen bonds in the systems analyzed have to take into account the orbital interactions between these two atoms along the molecular main axis. The main oxygen–metal interactions along the linear chain are both σ and π type, as shown in Fig. 1. This figure shows the orbital interactions between one titanium and two oxygen atoms. The oxygen–metal chain is here oriented along the z-axis; thus, the structural properties of the titanium–oxygen chain will be ruled by the extent of σ and π interactions between the metal d and p and oxygen p orbitals.

Preliminary calculations were performed on oligomers on both the syn and the anti structures, in order to check the relative stability of the two conformations. The anti conformation is always more stable than the syn conformation in all the systems considered, with an almost perfectly linear increase in the energy difference

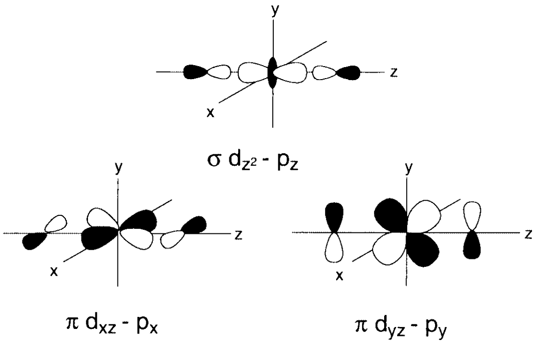


Fig. 1. Main bonding interaction for the titanium *d* and oxygen *p* orbitals along the molecular axis. The titanium atom lies at the origin of the coordinate system and the two first-neighboring oxygen atoms lie along the *z*-axis. One σ bonding interaction, along the molecule's principal axis, and two orthogonal π bonding interactions are shown

with the number of Ti–O units. This is in agreement with the experimental structures, where only the anti structure is observed [3]. The energy difference between the two conformations can be ascribed to the different sterical interactions among the aromatic rings. These contributes arise from the π–π stacking interactions between the ligands. This was confirmed by calculations on titanium–ligand fragments (positively charged), at the oligomer equilibrium geometries, omitting the bridging oxygen atom. A different topology in the syn and anti interactions corresponds to changes in the direct interaction between the aromatic ring *p* orbitals. In particular, the syn configuration allows a more extended antibonding interaction of electron-filled π orbitals, giving rise to an overall energy increase. The extent of this interaction will thus depend on the distance between the aromatic ring planes, which is related to the titanium–oxygen bond length along the oligomer axis; however, these interactions influence slightly the properties of the titanium–oxygen bond along the main axis. Because of the lower energy for the anti species, only this conformation will be considered hereafter.

The results for the geometry optimization of the species depicted in Scheme 1 ($n = 1, 2, 3$) and Scheme 2 ($n = 0, 1, 2$) are given in Tables 1, 2 and 3. Geometry optimizations were performed by imposing the constraint of C_{2v} or C_{2h} symmetry in the structures referred to in the tables as symmetric, and also by releasing this constraint in the structures referred to as asymmetric.

The optimized geometrical parameters related to the titanium–oxygen distances, along the molecule's main axis, for the neutral dimer depicted in Scheme 1 ($n = 1$) are shown in Table 1. The geometry optimization performed starting from an asymmetric structure for the dimer converged to a nearly symmetric molecule, indicating the C_{2h} symmetry as the more stable configuration for this species. This is in good agreement with the experimental structures, which indicate nearly perfect symmetry, with respect to the molecular center, for the titanium–oxygen distances.

The computed geometries were compared with the experimental structures by carrying out calculations, at the same level of theory, on dimers for which structural data are available. They differ from the series of oligomeric species considered by the presence of two chlorine atoms and two nitrate groups, respectively, substituting the hydroxilic terminal group. The results are reported in Table 1 and show good agreement between theoretical and experimental data. The calculations show only a slightly longer distance for the titanium–oxygen bond length, indicating an underestimate of the titanium–oxygen π interactions. Geometry optimizations carried out by adding polarization functions on the oxygen atoms along the chain lead to almost identical results.

Table 1. Selected optimized bond lengths (angstrom) for the species $[Ti(O{-}CH{=}CH{-}CH{=}NH)(X)]^2$ (μ_2-O) (X=OH,Cl, NO_3) in the symmetric configuration and for the ionic species **1** (Scheme 2 for $n = 0$) and **2** (Scheme 4)

	d(Ti–O)		*d*(Ti–*X*)	
	Theor.	Exp.	Theor.	Exp.
X = OH	1.856	–	1.850	–
X = Cl	1.863	1.813[a]	2.416	2.443[a]
X = NO_3	1.839	1.802[b]	2.065	2.137[b]
1	1.834	–	–	–
2	1.904/1.801	–	1.874	–

[a] Experimental value for $[Ti(acacen)(Cl)]_2(\mu_2\text{-}O)$ (from Ref. [4])
[b] Experimental value for $[Ti(acacen)(NO_3)]_2(\mu_2\text{-}O)$ (from Ref. [3])

Table 2. Optimized titanium–oxygen bond length (angstrom) for the neutral trimer (Scheme 1 for $n = 2$) in the symmetric and asymmetric configurations and the doubly ionized dimer (Scheme 2 for $n = 1$) (see text)

	C_{2v} ($d_i = d_{i'}$)	C_s ($d_i \neq d_{i'}$)	Cation	
			Theor.	Exp.[a]
d_1	1.854	1.851	2.227	(2.362)
$d_{1'}$	–	1.864	2.231	(2.172)
d_2	1.846	1.846	1.780	1.663
$d_{2'}$	–	1.838	1.782	1.786
d_3	1.873	1.884	1.956	1.974
$d_{3'}$	–	1.863	1.909	1.846

[a] Experimental values for $[Ti(salen)]_3(\mu_2\text{-}O)_2(tetrahydrofuran)_2$, (from Ref. [3])

Table 3. Optimized titanium–oxygen bond length (angstrom) for the neutral and the doubly ionized tetramers (scheme 2 for $n = 2$) in the symmetric configuration (see text)

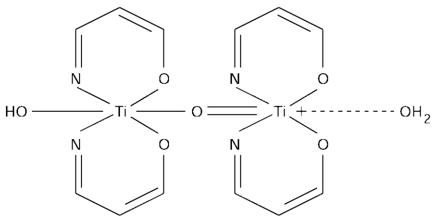
	Neutral Theor.	Cation	
		Theor.	Exp.[a]
d_1	1.896	2.273	–
d_2	1.852	1.743	1.714
d_3	1.904	1.987	2.036
d_4	1.879	1.843	1.822

[a] Experimental values for $Ti(acacen)_4(\mu_2\text{-}O)_3(tetrahydrofuran)_2$ (from Ref. [3])

Mixing coefficient analysis for molecular orbitals in the neutral dimers has shown low contributions for the metal d_π orbitals, confirming that the corresponding

Ti–O bonds are rather weak and strongly polarized toward the oxygen atom. As a result, the interaction between the two titanium atoms and the bridging oxygen consists mainly of a single σ bond with two weak π contributions.

Selected geometrical parameters concerning the dimeric cationic species are also shown in Table 1. Species **1** is the doubly charged solvated dimer ion, which corresponds to the molecule in Scheme 2 for n=0, while species **2** is the singly positively charged ion whose structure is shown in Scheme 4.



The shortening of the terminal Ti–O unit in the singly positively charged ion to 1.80 Å indicates an interaction with double-bond character. Indeed, while the high-energy d metal orbitals tend to form weak π bonds with the low-lying oxygen p orbitals when both the titanium atoms are in the neutral state, when one of the two titanium atoms is ionized, its d orbitals are lowered in energy and a π donation from oxygen to the positively charged titanium takes place, giving rise to an increase in the Ti–O bond π character. Moreover, the double ionization (complex **1**) does not affect significantly the bonding mode in the Ti–O–Ti unit; thus, species **2**, which can be viewed as the product of a single ionization process, contains a Ti=O unit that is weakly bound to the other titanium–acacen unit and can be considered as a starting reactant for the production of Ti=O building blocks.

The results of geometry optimization for the neutral trimer, performed within C_{2v} and C_s symmetry constraints, i.e. with and without the symmetry plane perpendicular to the molecular axis, are reported in Table 2. The geometrical parameters in the table correspond to titanium–oxygen distances according to the following scheme:

$$\begin{array}{ccccccccccccc} & d_1 & & d_2 & & d_3 & & d_{3'} & & d_{2'} & & d_{1'} & \\ \mathrm{HO} & — & \mathrm{Ti} & — & \mathrm{O} & — & \mathrm{Ti} & — & \mathrm{O} & — & \mathrm{Ti} & — & \mathrm{OH} \end{array}$$

For the neutral trimer both the symmetric and the asymmetric configurations show similar energies; however, in both cases, all the titanium–oxygen distances resemble those for a typical single Ti–O bond, as in the neutral dimer, confirming weak π character.

The optimized geometrical parameters for the doubly ionized solvated trimer, with the same bonding scheme, are also shown in Table 2. Calculations of bond lengths for the doubly ionized species have made possible more realistic comparisons with the experimental values. Although the average agreement between the computed and the experimental geometries is reasonable, the different terminal Ti–O bond lengths in the dication, corresponding to single and double titanium–oxygen bonds, respectively, is only poorly described by the optimized geometries, which give only slightly different bond lengths. Calculations performed with a more extended basis set on the oxygen atoms have shown the same deficiency.

The optimized geometrical parameters for the tetramer in the neutral and doubly charged state are shown in Table 3. The bond parameters are labeled according to the following scheme:

$$\begin{array}{ccccccccccccccccc} & d_1 & & d_2 & & d_3 & & d_4 & & d_4 & & d_3 & & d_2 & & d_1 & \\ \mathrm{HO} & — & \mathrm{Ti} & — & \mathrm{O} & — & \mathrm{Ti} & — & \mathrm{O} & — & \mathrm{Ti} & — & \mathrm{O} & — & \mathrm{Ti} & — & \mathrm{OH} \end{array}$$

For the tetramer, calculations have shown that the symmetric configuration is the most stable, as confirmed by experiment; thus, only results for this configuration are presented. Experimental data are available for the double ionized tetramer and the agreement is good at the generalized gradient approximation level of theory. As in the dimer and trimer cases, the tetramer bonding situation reflects single titanium–oxygen bonds, with only weak π contributions; however, these interactions extend along the whole oligomeric chain, as shown by the molecular orbital isodensity contours in Fig. 2.

The bond lengths reveal that in the neutral molecules, the central Ti–O distances tend to have an alternating trend increasing the chain length (1.85 Å for the dimer, 1.87 Å for the trimer and 1.84 Å for the tetramer). This trend has been confirmed by a geometry optimization for the neutral pentamer in which the resulting titanium–oxygen bond length for the central unit is 1.89 Å. However, these small differences show that for long-chain oligomers terminal groups do not have strong effects on the central units.

Calculations on polymeric complexes were carried out on systems having the following structure:

$$—(—\mathrm{Ti}—\mathrm{O}—\mathrm{Ti}—\mathrm{O}—)_n—$$

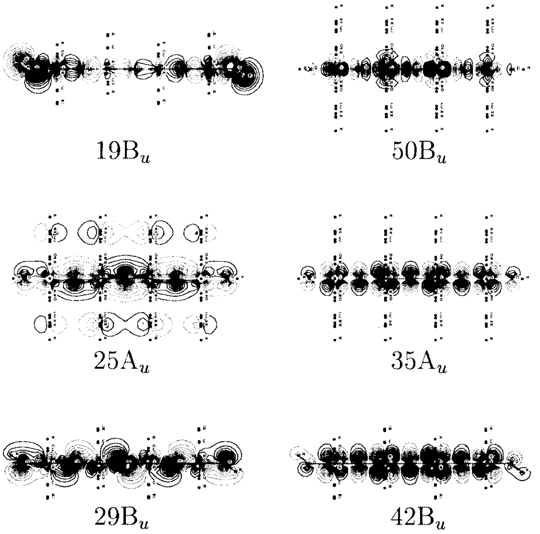


Fig. 2. Computed molecular orbitals (isodensity contours) for the neutral tetramer in the symmetric configuration (Scheme 1 for $n = 3$) corresponding to the σ and the two π interactions. Bonding orbitals on the *left*, antibonding on the *right*

with two titanium–oxygen units in the unit cell and the aromatic groups in the anti configuration.

The geometry optimization results for the Ti–O distance in extended systems give a bond length of 1.879 Å, in good agreement with the value for the tetramer central unit. The calculations did not show any Peierls distortion; then, the minimum energy conformation corresponds to a system with all Ti–O distances identical, as expected for these d^0 transition-metal polymeric complexes with a large band gap between the highest-occupied crystal orbital (HOCO) and the lowest-unoccupied crystal orbital (LUCO). The titanium–oxygen bond length shows the typical value for a single bond, confirming that π Ti–O interactions are only possible when there is a charge depletion on the titanium atom. The lack of terminal effects in the extended system does not allow, in fact, a different charge distribution for the titanium atoms along the chain; thus, the formation of the titanylic Ti=O unit cannot be observed.

These considerations can be confirmed by analyzing the polymer energy levels. PDOS and COOP make possible awarding of energy bands to specific orbitalic interactions. The results are shown in Figs. 3, 4 and 5.

The strong σ bond corresponds to the interaction between the titanium d_{z^2} orbitals and the oxygen p_z orbitals, and its PDOS and COOP are shown in Fig. 3a and b, respectively. The energy band corresponding to the bonding interaction lies in the region between −8 and −9 eV. Figure 4a and b shows PDOS and COOP for the first of the two titanium–oxygen π interactions depicted in Fig. 1, i.e. the $d_{xz} - p_x$ bond. The COOP diagram shows that both bonding and antibonding interactions lie around the frontier orbital energy range; in particular, the LUCO belongs to the antibonding energy band pertaining to this interaction. PDOS and COOP for the other π interaction ($d_{yz} - p_y$) are shown in Fig. 5a and b, respectively. It is possible to note that the energy range for the related bands lies in the same range of the former π interaction; they have, in fact, the same nature and the energy difference is only due to the symmetry lowering produced by the Schiff ligand. Moreover, the HOCO (corresponding to the Fermi energy) corresponds to the bonding energy band for this π interaction. Thus, the

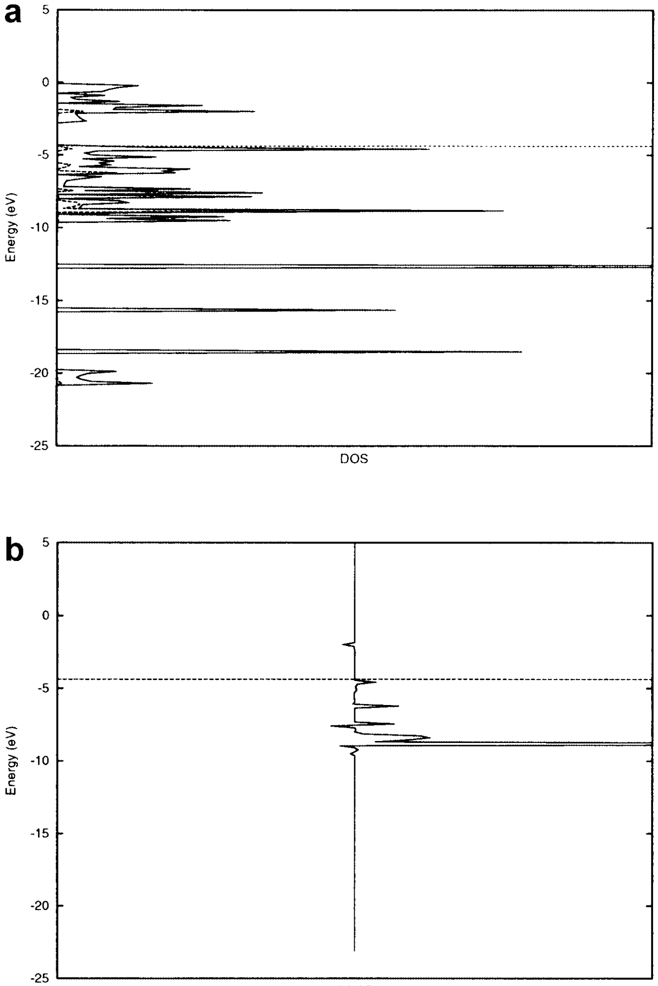


Fig. 3. **a** Total density of states (*solid line*) for the polymeric species and contributions (*dashed line*) from the titanium d_{z^2} and oxygen p_z orbitals. The *horizontal dashed line* indicates the Fermi energy. **b** Crystal orbital overlap population in the polymeric species for the titanium d_{z^2} and oxygen p_z orbitals

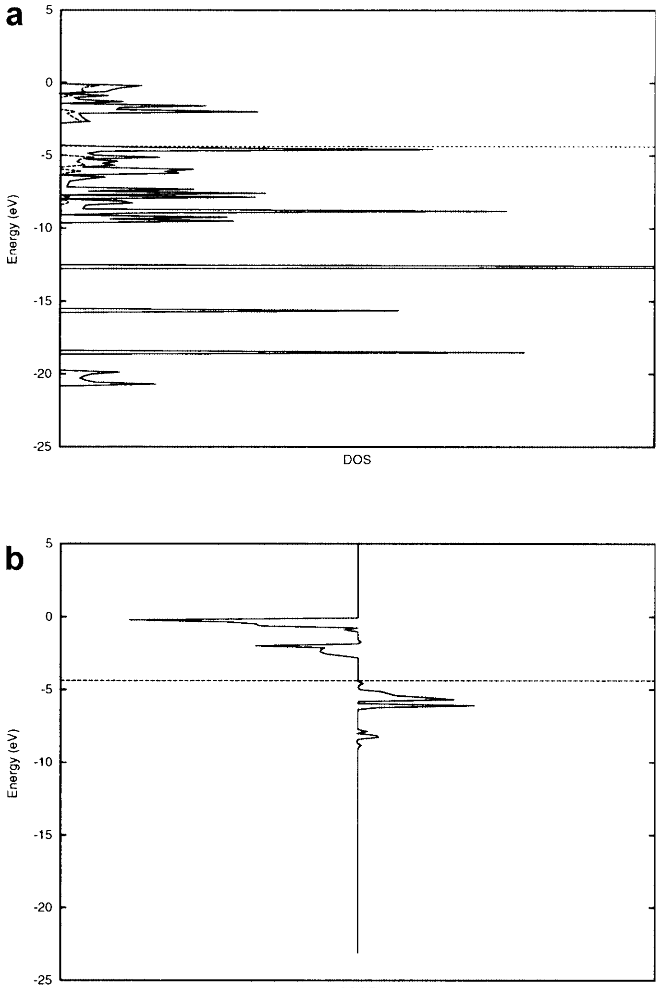


Fig. 4. **a** Total density of states (*solid line*) for the polymeric species and contributions (*dashed line*) from the titanium d_{xz} and oxygen p_x orbitals. **b** Crystal orbital overlap population in the polymeric species for the titanium d_{xz} and oxygen p_x orbitals

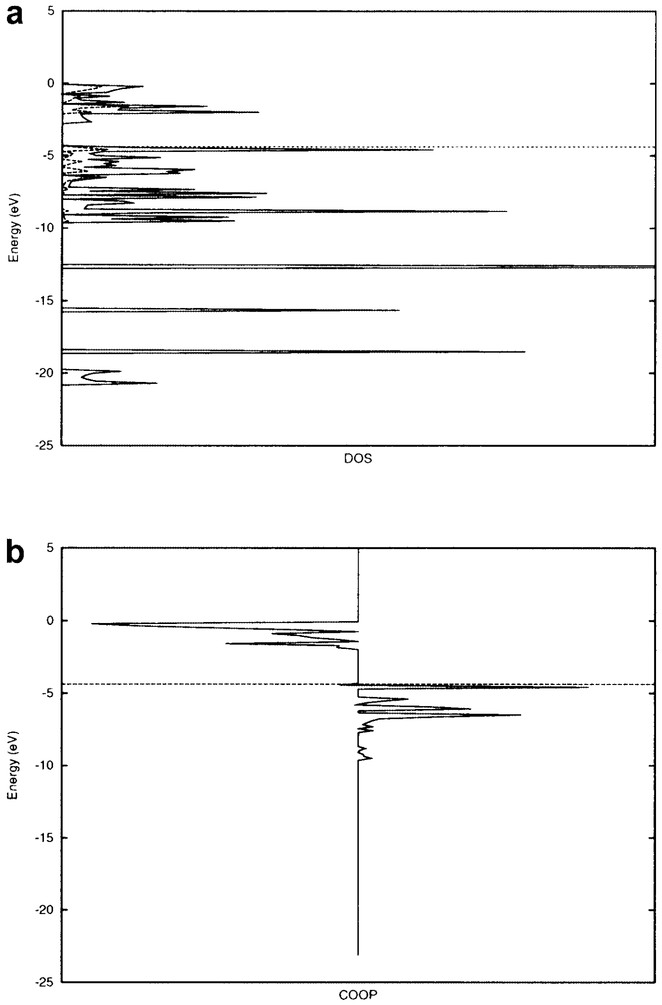


Fig. 5. **a** Total density of states (*solid line*) for the polymeric species and contributions (*dashed line*) from the titanium d_{yz} and oxygen p_y orbitals. **b** Crystal orbital overlap population in the polymeric species for the titanium d_{yz} and oxygen p_y orbitals

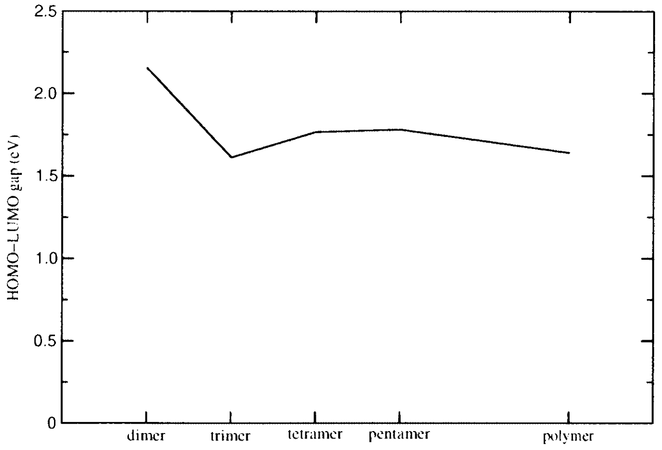


Fig. 6. HOMO–LUMO band gap (eV) for the oligomeric systems (Scheme 1 for n=1, 2, 3, 4) and the polymer

HOCO–LUCO band gap is 1.64 eV using the Becke88–Perdew86 gradient-corrected functional. These values can be compared with the HOMO–LUMO gap for oligomeric systems, as shown in Fig. 6. It is possible to see how the HOMO–LUMO gap for oligomers converges to the HOCO–LUCO polymer band gap on increasing the number of titanium–oxygen units. This confirms that the polymer frontier orbitals have similar properties to high-order oligomer ones. Moreover, calculations have shown that calculated polymer band energies are in good agreement with the oligomer energy levels. In particular, it has to be noted that the polymeric band structure is rather close to the tetramer energy level diagram, as shown in Fig. 7, especially for the frontier orbitals and for those concerning π-type interactions, confirming that the structural and the electronic properties of the extended systems are similar to those obtained for high-order oligomers.

5 Conclusions

In this work we investigated on the bonding modes of oligomeric and polymeric linear titanoxanes by means of DFT calculations. Our results give, in general, a good description of the titanium–oxygen bond properties for this class of compounds. In particular, the symmetry of

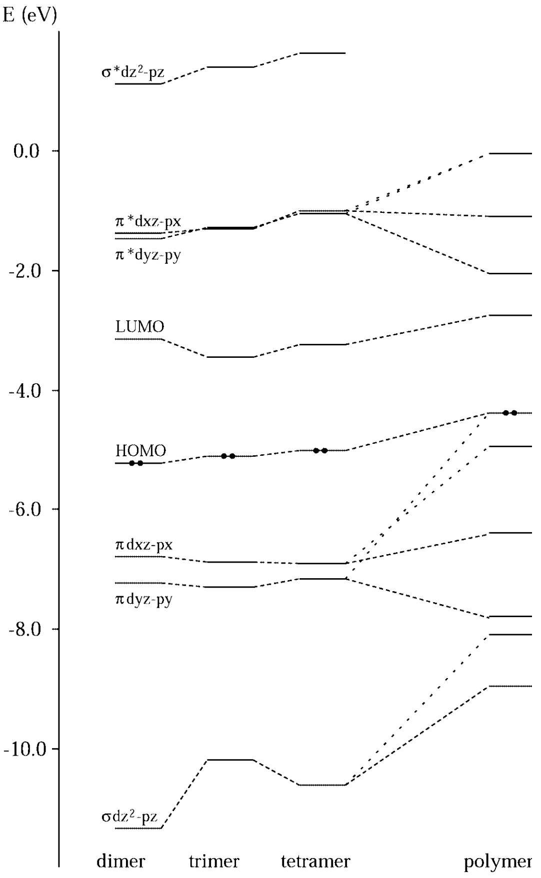


Fig. 7. Correlation diagram for the σ and π bonding and antibonding molecular orbitals with the HOMO and the LUMO for the oligomers and the polymer. The energy levels (molecular orbitals) for the oligomers correspond to the lowest (bonding) or highest (antibonding) crystal orbital of the energy bands in the polymer

the dimeric and the tetrameric species is well reproduced, and particularly also the asymmetryzation of the trimeric species, though differences between single and double bonds are not so pronounced. Moreover, the double ionization of these species does not affect substantially the bonding mode, confirming the single ionization process as the key step for the formation of the titanyl Ti=O unit.

As the chain length increases, the titanium–oxygen interactions tend to assume single-bond character. This is confirmed by the optimized structure for the polymer, where the Ti–O distance is very close to that found for the central unit in the tetramer. This also reflects similar electronic properties for high-order oligomers and polymers, especially as far as it concerns frontier orbitals.

From our investigations, we can also conclude that oligomers and polymers are strictly related, being characterized by common features concerning their electronic and structural properties; such investigations may then give strong support to the experimental results. Future developments may deal with systems where the titanium atom lies on a different electronic environment owing to the presence of other kinds of ligands.

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