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Structure and properties of dimer, trimer and tetramer aggregates of methyltrioxorhenium (MTO): an ab initio study

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Abstract

We have performed ab initio Hartree–Fock self-consistent field calculations on the electronic and geometric structure of methyltrioxorhenium (MTO) and its dimers, trimer and tetramer. This latter hypothetic compound has many features in common with the recently discovered polymeric form of MTO, poly-MTO, and the present results show that the tetramer provides a model for the interpretation of the IR and Raman spectra. Based on the tetramer, we also predict some unknown geometrical parameters of poly-MTO. The Re atoms in poly-MTO exhibit an electronic structure which closely resembles that of the Re atom in the monomer. The tetramer results suggest that the negatively charged bridging oxygen atoms in the polymeric form are the best candidates for binding the excess protons present in poly-MTO.

Keywords: Rhenium; Methyltrioxorhenium; Ab initio study; Vibrational spectroscopy

1. Introduction

Recently, the first example of the aggregation of an organometallic oxide to form a polymeric oxide still containing organic ligands was reported [1,2]. Starting from a diluted solution of H_3C-ReO_3, methyltrioxorhenium (MTO), the formation of a gold-colored precipitate with peculiar chemical and physical characteristics was observed. A careful study of this new material revealed the formation of a two-dimensional structure of polymeric MTO [2], comprised of layers of corner-sharing $ReO_5(CH_3)$ octahedra which then form staggered layers intercalated by water molecules. A considerable amount of acidic protons is diluted into the lattice [2].

This novel material is of great interest owing to its unprecedented composition and structure and the resulting chemical and catalytic properties. It was therefore interesting to study this material from a theoretical point of view in order to elucidate its electronic structure and properties. Extended Hückel band structure calculations

have been reported [3]. However, despite the very accurate experimental characterization of poly-MTO through X-ray diffraction and various analytical techniques [1,2], there are some structural and spectroscopic aspects of poly-MTO which are still open to theoretical interpretation. In particular, some of the geometrical parameters in the structure have not been determined because of the absence of X-ray reflections in some spatial directions.

In this study we have determined, by means of ab initio calculations, the geometric and electronic structures of some hypothetical compounds which may represent the initial steps in the polymerization of MTO. These structures include dimers, trimers and tetramers of MTO. This latter compound, "tetra-MTO", already shows a considerable resemblance to the periodic structure. The vibrational spectrum of tetra-MTO has been computed and compared with the IR and Raman data on poly-MTO. Finally, we have considered the changes in the electronic structure of the Re atoms as one goes from the isolated MTO monomer to the dimeric, trimeric and tetrameric compounds. It will be shown that, from an electronic structure point of view, poly-MTO has many features in common with the monomer MTO; the most important difference lies in the oxygen bridging

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the Re atoms which in poly-MTO show a strong nucleophilic character. These oxygens differ substantially from the terminal oxygens in MTO and poly-MTO.

2. Computational details

We have performed ab initio Hartree–Fock (HF) self-consistent field (SCF) calculations using a relativistic effective core potential (ECP) [4] for rhenium. Two different ECPs have been examined. The first includes in the valence shell the configuration $5s^2\ 5p^6\ 5d^5\ 6s^2$ for a total of 15 electrons; we call this ECP small core (SC). The second includes explicitly in the valence only the seven $5d^5$ and $6s^2$ electrons of Re, the remaining 68 electrons being in the core; we call this ECP large core (LC). The contracted Gaussian basis sets used for the SC and LC Re ECPs are [4s/4p/2d] and [2s/2p/2d] respectively [4]. The other atoms have been treated with all their electrons; the contracted basis sets are [4s/3p] for C and O [5] and [2s] for H [6].

It is well known that the HF approximation is inadequate for the accurate prediction of bond lengths of metal complexes and that correlation effects are needed in order to obtain better agreement with experiment. However, it has recently been shown that the HF approach works well for complexes involving transition metal atoms in high oxidation states [7]. This is the case for Re which in MTO is formally in its +VII oxidation state. To check the adequacy of the theoretical approach, we have determined the geometry of MTO (Fig. 1) at the HF level by means of analytical gradients and compared the results obtained with the LC and SC ECPs with those of all-electron scalar relativistic density functional (DF) calculations [8] and with experimental data [9] (Table 1). The HF results are in very good agreement with the experimental data as well as with the DF results. This finding also ensures that the relativistic ECP properly reproduces the typical contraction of the 6s orbital and the consequent expansion of the 5d shell. Furthermore, similar results are obtained
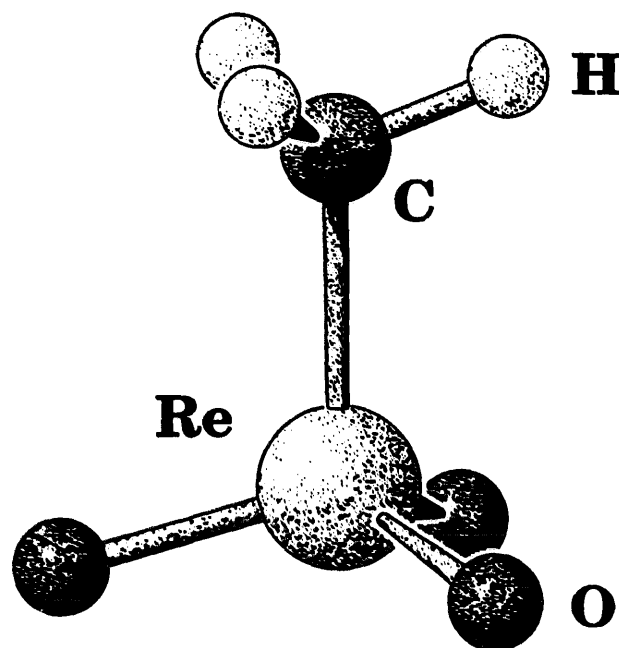

Fig. 1. The structure of methyltrioxorhenium, MTO.

with the SC and LC ECPs, the largest difference being for the Re=O bond (the SC ECP r_e is about 0.02 Å longer than the LC one). Therefore, the subsequent calculations of the oligomeric model systems have been carried out with the more economic LC effective core potential. All calculations have been performed with the HONDO program package, Version 8.5 [10].

3. Results and discussion

3.1. Geometrical structure

Three possible isomers of di-MTO are shown in Fig. 2. They correspond to local minima of the potential energy surface. The first structure (1) represents a natural building block of poly-MTO assuming that all the methyl ligands are oriented to the same side of the oxide layers; the relative orientation of the methyl groups

Table 1

Geometrical parameters of MTO computed by various theoretical approaches. Bond lengths d are given in Å, angles $<$ in degrees

	HF		DF [c]	Exp. [d]
	(LC–ECP) [a]	(SC–ECP) [b]		
d(Re–C)	2.11	2.10	2.02	2.06
d(Re–O)	1.67	1.69	1.71	1.71
d(C–H)	1.09	1.09	—	—
$<$ (C–Re–O)	104	103	103	106
$<$ (H–C–Re)	109	109	—	—
$<$ (H–C–H)	110	110	—	—
$<$ (O–Re–O)	115	115	114	113

[a] LC–ECP, large core effective core potential for Re (explicit treatment of $6s^2\ 5d^5$ [4]); this work. [b] SC–ECP, small core effective core potential for Re (explicit treatment of $5s^2\ 5p^6\ 6s^2\ 5d^5$ [4]); this work. [c] Density functional calculation using the local density approximation; Ref. [8]. [d] Experimental structure; Ref. [9].
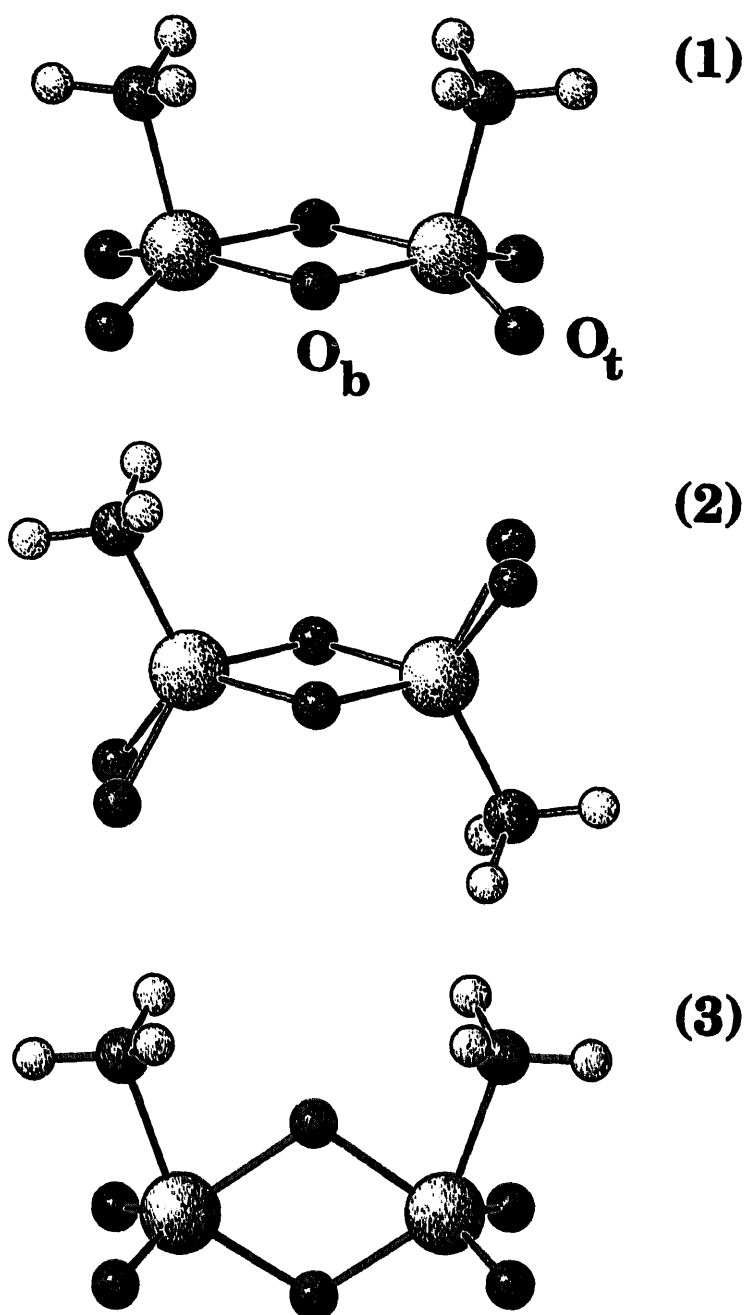
(1)

(2)

(3)

Fig. 2. Computed structures of MTO dimers 1, 2, 3, see also Table 2.

Table 2
Geometrical parameters of MTO and of the polymerization models 1–5. Bond lengths d are given in Å, angles $<$ in degrees (see Figs. 1 to 3)

	1	2	3	4	5
d(Re–Re)	3.26	3.08	3.24	3.84	3.83
d(Re–C)	2.09	2.04	2.14	2.11	2.11
d(C–H)	1.09	1.09	1.09	1.09	1.09
d(Re–O_t)	1.65	1.89	1.65	1.66	1.66
d(Re–O_b)	1.98	1.93	1.97	1.95	1.94
$<$ (C–Re–O_t)	103	120	105	100	100
$<$ (C–Re–O_b)	101	111	108	100	99
$<$ (O_b–Re–O_t)	90	97	113	88	88
$<$ (O_b–Re–O_b)	69	75	69	78	80
$<$ (Re–O_b–Re)	111	106	111	162	168

in poly-MTO is not known precisely [2]. In this structure (1) all the bridging oxygen atoms and the Re atoms lie essentially in one plane, with the CH_3 groups perpendicularly bonded to the Re atoms in a *cis* orientation. By changing the orientation of the CH_3 group the *trans* isomer 2 is obtained. This second structure, however, is about 270 kJ mol^{-1} higher in energy than 1. Although some care is required in commenting on relative stabilities obtained at the HF level, this is a relatively large energy difference which seems to indicate a preference for the methyl groups being all on the same side of the molecule. Neither 1 nor 2, however, are the most stable isomers of the MTO dimer. In fact, we found a third structure (3) which is about 95 KJ mol^{-1} more stable than 1, see Fig. 2. In this structure the bridging oxygen atoms form a plane with the Re atoms as well as with the CH_3 ligands. This structure, which clearly is not a precursor of poly-MTO, is reminiscent of that of $[(\eta^5\text{-}C_5Me_5)Re(\mu\text{-}O)Cl_2]_2$ [11], a dimeric complex of Re(V) where the ligand stereochemistry is exactly as found in 3. Another possible isomer corresponding to 3, but with a *trans* orientation of the methyl groups, has been considered. However, we were unable to achieve convergence in the SCF

procedure, which may indicate a low stability of the structure. In all three structures the Re–Re distance is very long, 3.1–3.2 Å (Table 2), suggesting that no Re–Re interaction is present. Another dimeric form of methylrhenium oxides is known to have the formula $[ReO_2(CH_3)_2]_2$ [12] and a structure not too different from that of 3, except for the presence of a methyl group which replaces an oxygen ligand. In $[ReO_2(CH_3)_2]_2$ the Re–Re distance is 2.59 Å, i.e. much shorter than in the dimeric structures considered here. However, this is not surprising given the fact that in $[ReO_2(CH_3)_2]_2$ Re is in a +VI oxidation state and not in a +VII state as in di-MTO. Thus, in $[ReO_2(CH_3)_2]_2$, one electron is available on each Re center to form an Re–Re bond, in contrast to the situation in di-MTO investigated here.

Substantial differences are found in the $Re-O_t$ and $Re-O_b$ distance of 1, 2 and 3 where the subscripts indicate terminal and bridging oxygens respectively. In particular, 2 shows a very long $Re-O_t$ distance, at variance with 1 and 3. In all cases the $Re-O_b$–Re angle is around 105–110°, quite typical for oxygen compounds.

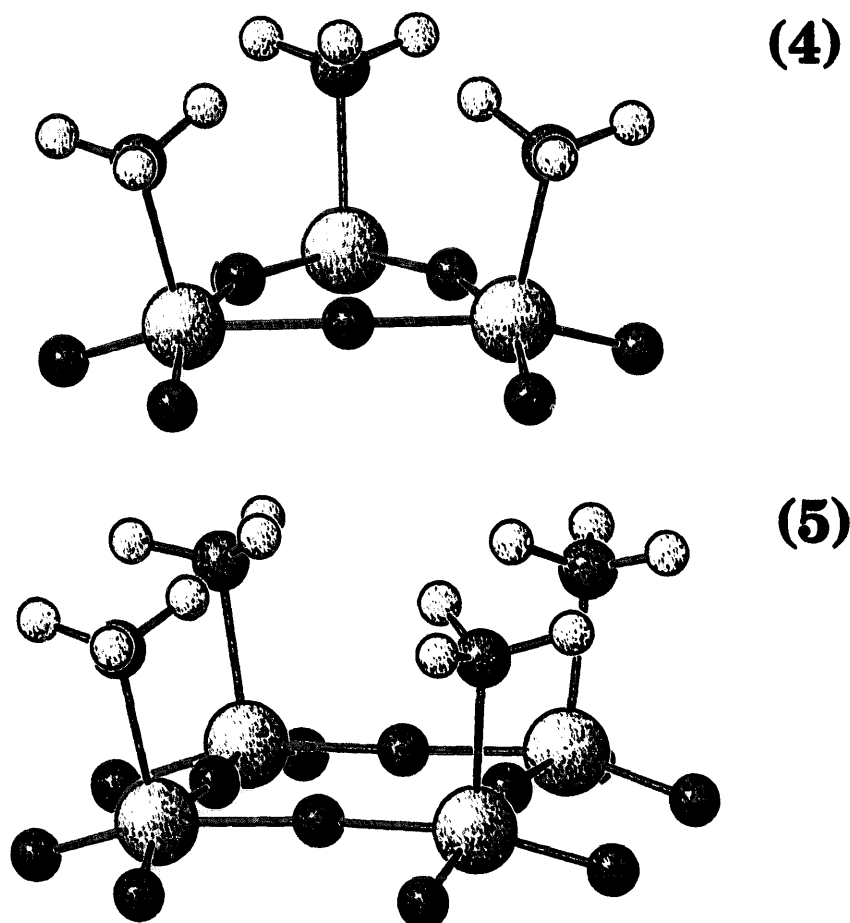The trimeric (4) and the tetrameric (5) forms of MTO

(4)

(5)

Fig. 3. Computed structures of the MTO trimer 4 and the tetramer 5, the latter representing a section of an idealized structure of poly-MTO.

Table 3
Calculated and experimental (IR and Raman (RA)) vibrational frequencies (cm^{-1}) and intensities (int.) of MTO

| Irrep. [a] | Frequency | | | Int. [b] | Assignment | |
| | Calc. [c] | Exp. [b] | | | Exp. | Calc. |
		IR	RA			
e	3016	2984	2985	vw	ν_7	100% $\nu(CH)_{as}$
a	2832	2902	2898	w	ν_1	99% $\nu(CH)_{sym}$
e	1323	1368	1375	w	ν_9	92% $\delta(CH_3)_{as}$
a	1273	1205	1206	vw	ν_4	98% $\delta(CH_3)_{sym}$
a	1002	998	995	m	ν_2	96% $\nu(ReO)_{sym}$
e	929	965	960	vs	ν_8	58% $\nu(ReO)_{as}$
e	837	736	740	w	ν_{10}	99% $\gamma_{rock}(CH_3)$
a	632	567	572	w	ν_3	95% $\nu(ReC)$
e	316	324	326	m	ν_{11}	92% $\delta(ReO_3)_{as}$
a	266	262	276	w	ν_5	90% $\delta(ReO_3)_{sym}$
e	248	253	252	w	ν_{12}	100% $\gamma_{rock}(ReO_3)$
a	237	241	240	w	ν_6	100% γ

[a] Irreducible representation: a, one-dimensional; e, two-dimensional. [b] Ref. [9]. [c] This work.

are shown in Fig. 3, they both represent local minima of the potential energy surface. Only structures where all the methyl groups are on the same side of the Re–O plane have been considered. Already the optimized structure of the trimer 4 starts to resemble that of poly-MTO; this resemblance is even more pronounced for the tetramer 5. Of course, as one goes from the dimer to the tetramer, the Re–O$_b$–Re angle increases and approaches the value of 170° which has been assumed for the two-dimensional structure [2] (Table 2). However, the true value (or its range) of the Re–O$_b$–Re angle in poly-MTO is not known. The value of the Re–O$_b$–Re angle is 162° and 168° in 4 and 5 respectively (Fig. 3), suggesting the preference for a non-linear Re–O–Re coordination. In systems related to poly-MTO, such as HWO$_3$ and HReO$_3$, the M–O–M units seem to be slightly bent with angles of about 170° [13,14]. The present calculations support this view. The

Re–Re distance in tetra-MTO, 3.83 Å, is reasonably close to that of poly-MTO, 3.73 Å [2]. The Re=O and Re–C terminal distances in poly-MTO are not known experimentally, although they are assumed to be close to the monomer values [2]. Indeed, the computed Re=O and Re–C distances in tetra-MTO, 1.66 Å and 2.11 Å respectively (Table 2), are very close to those for the monomer (Table 1). This agrees with the experimental data which are consistent with only a weak modification of the internal structure of MTO upon polymerization [1,2].

3.2. Vibrations

Before we discuss the vibrational properties of tetra-MTO, we will briefly comment on the reliability of the computed vibrational frequencies in the HF approximation. To this end, the vibrational energies and intensities

Table 4
Calculated vibrational frequencies (cm^{-1}) of tetra-MTO 5 and IR and Raman (RA) spectra of poly-MTO

| Sym. [a] | Frequency | | | Int. [b] | Assignment [c] |
| | tetra-MTO | poly-MTO [b] | | | |
	Calc. [c]	IR	RA		
b$_1$	927	—	990	vs	$\nu_{as}(Re=O)$
e	875	—	—	—	ν Re=O)
a$_1$	828	912	912	sh	$\nu_s(Re=O)$
e	801	851	860	sh	$\nu(Re=O)$
e	713	758	760	m	$\delta(C-Re=O), \gamma_{rock}(CH_3)$
a$_2$,b$_1$	640	—	—	—	$\delta(C-Re=O), \gamma_{rock}(CH_3)$
a$_1$	532	550	560	vvw	$\nu_s(Re-C)$
b$_2$	513	—	—	—	$\gamma_{rock}(CH_3)$
a$_1$	472	494	480	sh	$\delta(C-Re=O)$
b$_2$	461	—	—	—	$\nu_{as}(Re-C)$
b$_1$	432	—	448	m	$\nu_{as}(Re-C)$
e	405	—	408	vs	$\delta(O=Re=O)$
a$_1$	356	—	323	s	$\delta_s(O=Re=O)$
b$_2$	350	—	—	—	$\delta_{as}(O=Re=O)$
b$_1$,a$_2$	329	343	340	sh	γ_{tors}

[a] Irreducible representation. [b] Ref. [9]. [c] This work.

of MTO derived from analytical second derivatives of the potential energy have been compared with experimental data [9] (Table 3). As usual, the HF method results in too large vibrational energies [15]. A much better agreement with the experimental data may be obtained by uniformly scaling all the force constants by a constant factor of 0.9 [15]. This factor has been used throughout the paper for the comparison of theoretical and experimental vibrational spectra. For MTO the agreement between calculated and measured values may be considered satisfactory (Table 3), with an average error of 37 cm^{-1}.

The experimental vibrational spectrum of poly-MTO resembles that of the monomer [1,9]. However, the splitting of many signals indicates a weak interaction between the layers in the polymeric form. From the analysis of the Raman spectra it was concluded that the IR-inactive Re–C and Re=C b_1 stretching frequencies are indicative of a local C_{4v} symmetry around Re in poly-MTO [1].

The vibrational spectrum of tetra-MTO (Table 4) has been calculated with some constraints. In particular, the methyl groups and the basic fragment consisting of Re and the bridging O atoms were kept fixed (the vibrations of the Re–O–Re skeleton occur at too low frequencies to the observed experimentally). Similarly to the monomer, the computed vibrational spectrum of tetra-MTO is divided into four regions. The C–H stretching frequencies are found around 2900 cm^{-1}, ν(Re=O) is at about 1000 cm^{-1}, while the Re–C stretching vibrations (530 cm^{-1}) and the Re=O bending vibrations (350 cm^{-1}) are found at lower frequencies. These latter modes are not pure and are strongly mixed with other skeletal torsions and deformations (Table 4). However, the two modes which are the most relevant for the IR characterization, namely the Re–C and Re=O stretchings, are largely pure modes with little admixtures of other modes. The vibration ν_{as}(Re–C) occurs at 432 cm^{-1} (exp. 448 cm^{-1}) and the vibration ν_{as}(Re=O) at 927 cm^{-1} (exp. 990 cm^{-1}). The experimentally observed additional splitting of the corresponding totally-symmetric modes is not reproduced

by the HF calculations. This leads to the conclusion that this splitting originates from the weak interaction of the layers in the three-dimensional poly-MTO structure. Thus, the structure proposed for poly-MTO [1], ReO$_2$ planes with methyl groups and oxygen atoms directly bound on opposite sides of the plane, is supported.

3.3. Electronic structure

The previous discussion has shown that both the geometrical parameters and the vibrational modes suggest a close similarity of the electronic structure of MTO to that of the polymeric form; in particular, the Re–C and Re=O distances and frequencies in MTO and tetra-MTO are indicative of a similar electron distribution around the Re atom. To better characterize the electronic structure of the dimeric, trimeric and tetrameric forms of MTO we used two quantities, the core level ionization potentials (IPs) of the C 1s and O 1s levels and the atomic charges as derived from the Mulliken population analysis. The use of an ECP for the Re atoms prevents us from analyzing the core levels of the metal atom. This is unfortunate since core levels do provide a way to measure changes in the chemical environment directly related to experimental observables. In this paper the core level IPs are determined according to Koopmans' theorem (KT) as the inverse of the eigenvalue associated to a given orbital. While KT IPs are very different from measured ones because of the lack of electron relaxation, KT shifts are usually reliable as a qualitative indication of changes in the electronic structure [16]. However, Mulliken charges are not always reliable and are used here mainly for comparative purposes.

The C 1s level of the CH$_3$ group in MTO and its polymeric forms is shifted by about 2 eV to higher binding energies with respect to methane, 305.1 eV (Table 5). This suggests that the electronic charge of C is reduced compared with CH$_4$ and not increased as the formal oxidation state of Re, +VII, would imply. However, the C 1s IP remains rather constant in all the compounds considered here (Table 5), the largest devia-

Table 5
Carbon and oxygen 1s core level energies (eV) and Mulliken charges q (a.u.) of MTO and of the models 1 to 5

	MTO	1	2	3	4	5
C 1s	−307.2	−307.6	−307.1	−307.0	−307.4	−307.4
O$_t$ 1s [a]	−561.8	−562.2	−561.9	−562.4	−561.8	−561.7
O$_b$ 1s [a]	—	−559.9	−560.5	−560.9	−559.6	−559.4
				−559.9		
q(C)	−0.67	−0.62	−0.81	−0.47	−0.59	−0.59
q(O$_t$) [a]	−0.57	−0.45	−0.43	−0.49	−0.45	−0.46
q(O$_b$) [a]	—	−0.96	−0.84	−0.97	−1.04	−1.05
				−0.94		
q(Re)	1.67	1.74	1.72	1.74	1.84	1.84

[a] Terminal (O$_t$) and bridging (O$_b$) oxygen atoms; see text.

tions being of the order of 0.6 eV. The O 1s IPs provide a clear indication of the very different nature of the terminal and bridging oxygen atoms in poly-MTO; in fact, the 1s level of bridging oxygen atoms is shifted to smaller IPs (by 1.5–2.5 eV) compared with the terminal ones. For comparison, the O 1s level in water is computed at 559.5 eV, i.e. in exactly the same region as the bridging oxygen atoms (Table 5). The different chemical nature of O_t and O_b is also reflected in the Mulliken charges which, for the bridging oxygen atoms, are two times larger than for the terminal ones.

The peculiar nature of the bridging oxygens compared with the terminal ones appears already in the dimers, and is found unchanged in the tetramer and, presumably, in poly-MTO. This suggests that the bridging oxygens have a much more basic character than the terminal ones and thus can be the preferred centers for binding excess protons. A direct proof of this basicity difference may be obtained by computing proton affinities. However, the addition of a single proton implies a drastic reduction of the symmetry, rendering the calculations very demanding. In contrast, the reaction of $[(\eta^5\text{-}C_5Me_5)ReO_2]_2$ with HBF_4 leads to a protonation of the bridging oxygens with the formation of $\{[(\eta^5\text{-}C_5Me_5)Re(\mu\text{-}OH)(=O)]_2\}^{2+}$ [11]. This is an important point as the presence of acidic protons in poly-MTO has recently been demonstrated by solid state ^1H-NMR spectroscopy [1,2]. The clear difference in the charges of the bridging and terminal oxygens makes it likely that the formation of OH groups will occur preferentially at the former sites, at variance with the predictions of extended Hückel calculations [3].

The charge of Re never exceeds + 1.8 a.u., i.e. it is much smaller than the formal oxidation number, and remains stable as one proceeds from the monomer to the tetramer. However, this further supports the view that the electronic structure of Re atoms in poly-MTO is only slightly modified with respect to that of MTO. It also shows that the Re–C and in particular the Re=O bonds have a much higher covalent character than one would expect on the basis of the formal oxidation numbers.

4. Conclusions

According to ab initio HF quantum–chemical calculations, the electronic structure of tetramers of MTO is considered as a model for studying the properties, mainly geometrical and vibrational, of the real polymeric material poly-MTO. The results clearly show that the formation of the polymer does not significantly change the characteristic electronic structure of the monomer MTO. In fact, the Re–C and Re=O distances, the vibrational modes, and also the C and O 1s core level binding energies, remain practically unchanged as one grows the polymer from the monomer. The major difference is the appearance of a new type of oxygen atom bridging the Re atoms. These bridging oxygen atoms are found to form slightly bent Re–O–Re bonds and to have a character similar to that of the oxygen atom in a water molecule. These oxygen atoms are good candidates to bind the rather large number of acidic protons present in poly-MTO.

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