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Theoretical Study of the 1:1 and 2:1 (Homo- and Heterochiral) Complexes of XOOX′ (X, X′ = H, CH₃) with Lithium Cation

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ABSTRACT: A theoretical study of the 1:1 and 2:1 complexes of XOOX′ (X, X′ = H, CH₃) with the lithium cation has been carried out by means of ab initio computational methods up to the MP2/aug-cc-pVTZ level. The optical rotatory power and NMR parameters (absolute chemical shielding and indirect coupling constants) have been calculated. In addition, the racemization barriers within the complexes formed have been evaluated. Special attention has been paid concerning the differences between the 2:1 homo- and heterochiral complexes.
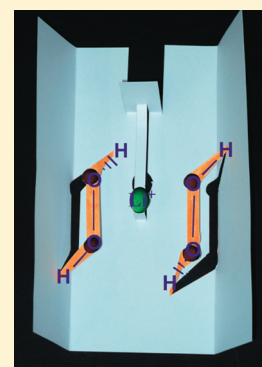
■ INTRODUCTION

The use of metallic atoms in chiral recognition processes and chiral catalysts has became one of the most interesting topics in the chemistry field.[1−3] One of the first applications involved the use of catalytic complexes in reduction processes that lead to what is known as nonlinear effects.[4,5] In the field of mass spectroscopy, several groups have used charged metals to bring together chiral entities and study the different stability of diasteromeric complexes.[6−8] The complexation of chiral transition metal moieties is of great interest in the colorimetric assessment of enantiopurity,[9] resolution of racemic alkenes, and NMR distinction of enantiomers.[10]

Even though up until now, most of the studies concerning chiral distinction (or chiral recognition) involving metals have been based on experimental approaches, some of us have also published several computational studies on the chiral distinction where charged metallic atoms were present. For instance, lithium complexes of bis(5H-pyrroles), bis(oxazolines),[11] difuranes[12] and 1-azahelicenes[13] as well as the complexes formed between hydrazine and metal atoms of group 10 have been examined.[14−16] In addition, the chiral distinction of chromium(0) complexes where hydrogen bond interactions were possible has been studied.[17]

Hydrogen peroxide and its derivatives have been widely used as models to computationally study chiral properties due to their small size, which makes them very adequate for theoretical studies. Thus, their optical rotatory power (ORP) shows a very interesting dependence on the dihedral angle, providing both positive and negative values in the range 0−180°.[18,19] The atomic partition of the ORP has been carried out using the acceleration gauge for the electric dipole and the torque formalisms.[20,21] The chiral discrimination of the dimers (homochiral vs heterochiral) has been previously studied for several of its derivatives (HOOX, X = H, C≡CH, CH₃, CF₃, t-C₄H₉, CN, F, Cl)[22,23] and for large clusters of the parent compound.[24,25] The coupling constants of some dimers have been calculated to check the possibility of this property to distinguish between homo- and heterochiral complexes.[26] The inclusion of the solvent effect on the chiral discrimination on the dimers of hydrogen peroxide and its methyl derivatives showed that their relative stability could be reversed due to solvation.[27,28]

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Scheme 1. Hydrogen Peroxide and Its Methyl Derivatives
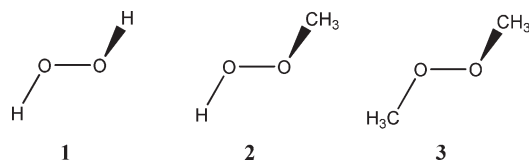
Table 1. Bond Distances (Å) and Angles (deg) of the Isolated Monomers[a]

molecule	O—O	X—O	XOO	XOOX
HOOH (**1**)	1.454	0.967	99.60	112.6
	1.475[45]	*0.950*	*94.8*	*119.8*
CH$_3$OOH (**2**)	1.456	0.958[b]/1.416[c]	99.32[d]/104.99[e]	119.59
CH$_3$OOCH$_3$ (**3**)	1.465	1.414	103.43	180.00
	1.457[42]	*1.420*	*105.2*	*119*

[a] The theoretical results have been obtained at the MP2/aug-cc-pVTZ computational level. The available experimental values are given in italics. [b] OH distance. [c] OC distance. [d] OOH angle. [e] OOC angle.

In the present article, the 1:1 and 2:1 complexes formed between hydrogen peroxide, two of their derivatives (Scheme 1) and the lithium cation have been considered, their spectroscopic properties (ORP, NMR shielding, and coupling constants) studied, and the barrier for the racemization of the molecules within the complexes analyzed.

■ METHODS

All the systems have been optimized at the MP2/6-31+G (d,p) computational level[29,30] and frequency calculations have been carried out at the same level to confirm that the structures obtained correspond to energetic minima or true TS. A further optimization has been carried out for the minima structures at the MP2/aug-cc-pVTZ computational level.[31] The interaction energy has been calculated as the difference between the energy of the complex and the sum of the isolated monomers. The ORP have been evaluated at the B3LYP/aug-cc-pVTZ level using the geometries optimized with the MP2/aug-cc-pVTZ method. This level of calculation has been considered adequate to obtain reliable results for this property based on a comparative analysis of a number of experimental and computational results.[32] The absolute chemical shieldings have been calculated with the GIAO method[33] at the MP2/aug-cc-pVTZ computational level. All these calculations have been performed with the Gaussian-03 package.[34]

In the Ramsey approximation, the total coupling constant (*J*) is a sum of four contributions: the paramagnetic spin—orbit (PSO), diamagnetic spin—orbit (DSO), Fermi-contact (FC), and spin-dipole (SD).[35] The SOPPA method[36−38] using the Ahlrichs[39] qzp basis set on ^{13}C, and ^{17}O, and the qz2p basis set on the ^{1}H have been used to compute the coupling constants. Because an Ahlrichs qzp basis set is not available for ^{7}Li, a previously constructed basis set was used for this atom,[40] which has the same number of contracted functions (6s, 4p, and 1d) as the Ahlrichs qzp basis has for C, and O. These calculations have been performed using the Dalton program.[41]
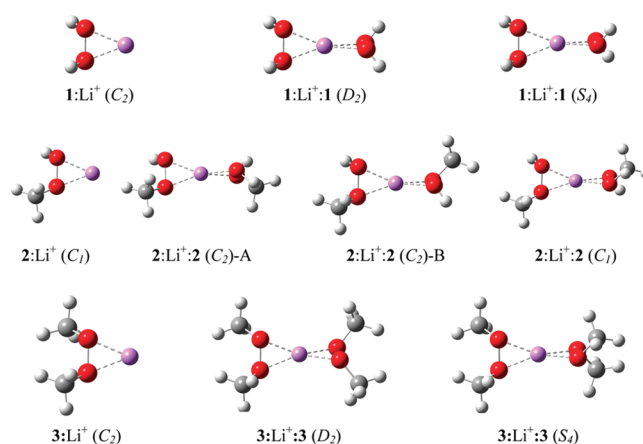

Figure 1. Optimized geometries of the 1:1 and 2:1 complexes at the MP2/aug-cc-pVTZ level. The symmetry of each system is indicated.

■ RESULTS

Energy and Geometry. The calculated geometries of the isolated monomers and their previously reported geometries in the gas phase have been gathered in Table 1. The geometry of **1** is adequately reproduced by the calculations while **3** is predicted to be planar even though the experimental data indicate that the COOC dihedral angle of this molecule is 119(10)°.[42] Previous studies have shown the difficulties to reproduce the experimental geometries of this molecule.[43,44] In the case of compound **2**, no experimental geometry has been reported.

The different complexes here studied formed by the hydrogen peroxide derivatives with the lithium cation are displayed in Figure 1. A unique 1:1 complex of **1** and **3** has been considered with C_2 symmetry. Two 2:1 complexes have been characterized for **1** and **3** and three for **2**. For the 2:1 complexes of **1** and **3**, a complex with D_2 symmetry where the two peroxide derivatives show the same XOOX dihedral angle in both molecules and consequently the chirality of both molecules is the same. This complex corresponds to the homochiral 2:1 complex. In the second complex the two molecules show the same absolute value of the dihedral angle but one is negative and the other positive. This complex presents S_4 symmetry and corresponds to the heterochiral 2:1 complex. The 1:1 complex of **2** has C_1 symmetry. Three 2:1 complexes have been found for this molecule, two with C_2 symmetry, which corresponds to homochiral complexes, and one with C_1 symmetry corresponding to the heterochiral one.

The calculated interaction energies of the complexes are gathered in Table 2. Those obtained at the MP2/6-31+G(d,p) computational level are around 2−6% larger than those obtained with the MP2/aug-cc-pVTZ computational method. However, similar relative energies are found with the two methods when the homo- and heterochiral complexes are compared.

Large interaction energies are obtained for the complexes formed between water peroxide derivatives and the lithium cation. It is interesting to notice that interaction energy increases in absolute value with the number of methyl groups present in the molecules involved. A similar tendency is observed in the protonation of these molecules and in fact a linear correlation is found between these two parameters in the three molecules considered ($R^2 = 0.999$).

The interaction energy of the 2:1 complexes is almost twice that of the corresponding 1:1 cluster. Thus, it can be said that

Table 2. Interaction (E_i) and Relative (E_{rel}) Energies (kJ mol^{-1}) and Bond Distances (Å) of the Complexes Calculated at the MP2/aug-cc-pVTZ Computational Level

system	E_i	E_{rel}	Li—O	O—O	O—X
1					
HOOH				1.454	0.967
HOOH:Li$^+$ (C_2)	−139.12		1.976	1.459	0.967
HOOH:Li$^+$:HOOH (D_2)	−256.61	0.52	2.009	1.460	0.972
HOOH:Li$^+$:HOOH (S_4)	−257.13	0.00	2.007	1.460	0.972
2					
CH$_3$OOH				1.456	0.968/1.416
CH$_3$OOH:Li$^+$ (C_1)	−157.49		1.950	1.467	0.974/1.444
CH$_3$OOH:Li$^+$: CH$_3$OOH (C_2-A)	−285.57	0.62	1.990^a	1.465	0.973/1.439
CH$_3$OOH:Li$^+$: CH$_3$OOH (C_2-B)	−285.64	0.55	1.990^a	1.465	0.973/1.440
CH$_3$OOH:Li$^+$: CH$_3$OOH (C_1-A)	−286.19	0.00	1.989^a	1.465^a	0.973/1.439^a
3					
CH$_3$OOCH$_3$				1.465	1.414
CH$_3$OOCH$_3$:Li$^+$ (C_2)	−171.00		1.929	1.476	1.442
CH$_3$OOCH$_3$:Li$^+$: CH$_3$OOCH$_3$ (D_2)	−306.30	0.73	1.976	1.472	1.437
CH$_3$OOCH$_3$:Li$^+$: CH$_3$OOCH$_3$ (S_4)	−307.04	0.00	1.974	1.472	1.437

^{a} Average values.

Table 3. $[\alpha]_D$ (deg) Calculated at the B3LYP/aug-cc-pVTZ//mp2/aug-cc-pVTZ Computational Level and XOOX$'$ Dihedral Angle (deg) for Each System

	$[\alpha]_D$	XOOX$'$ angle
HOOH	49.01	−112.6
	(45.73)^a	−119.8^a
HOOH:Li$^+$	30.62	−101.2
HOOH:Li$^+$:HOOH (D_2)	−13.26	−102.6
CH$_3$OOH	−165.27	−119.6
CH$_3$OOH:Li$^+$	−63.48	−95.4
CH$_3$OOH:Li$^+$: CH$_3$OOH (C_2-A)	−80.7	−98.7
CH$_3$OOH:Li$^+$: CH$_3$OOH (C_2-B)	−89.3	−98.9
CH$_3$OOCH$_3$	0.00	180.0
	(−566.85)^a	−119.0^a
CH$_3$OOCH$_3$:Li$^+$	−339.5	−95.6
CH$_3$OOCH$_3$:Li$^+$: CH$_3$OOCH$_3$ (D_2)	−354.4	−99.7

^{a} Based on the experimental geometry reported in Table 1.

Table 4. Absolute Chemical Shieldings (ppm) Calculated at the MP2/aug-cc-pVTZ Computational Level for Each Molecule (1, 2, and 3) and Corresponding Complexes

nuclei	1	1:Li$^+$	1:Li$^+$:1 (D_2)	1:Li$^+$:1 (S_4)
Li		93.77	92.88	92.89
O	152.67	158.35	157.98	158.16
	(150.77)^a			
H	24.73	22.84	23.08	23.07
	(24.59)^a			

nuclei	2	2:Li$^+$	2:Li$^+$:2 (C_2-A)	2:Li$^+$:2 (C_2-B)	2:Li$^+$:2 (C_1)
Li		93.63	92.80	92.83	92.82
OCH$_3$	133.24	114.76	120.13	119.68	119.83
OH	96.87	110.30	109.09	109.30	109.41
OH	23.79	22.58	22.77	22.76	22.74
C	130.97	123.40	125.07	125.04	125.00
H av^b	27.82	27.09	27.22	27.22	27.22

nuclei	3	3:Li$^+$	3:Li$^+$:3 (D_2)	3:Li$^+$:3 (S_4)
Li		93.44	92.77	92.74
O	85.92	75.31	78.74	78.48
	(81.62)^a			
C	133.75	129.38	130.58	130.45
	(133.56)^a			
H av^b	27.87	27.24	27.37	27.37
	(27.86)^a			

^{a} Based on the experimental geometry reported in Table 1. ^{b} Average value of the hydrogen atoms of the CH$_3$ moiety.

the 2:1 complexes are anticooperative with respect to the 1:1 ones. The heterochiral complex is always more stable than the corresponding homochiral one but the energetic differences are always smaller than 1 kJ mol^{-1}.

The geometrical parameters of the complexes have been reported in Table 2. The Li—O distance is the most sensitive parameter to the stereochemistry of the complex formed (1:1 or 2:1) and to the number of methyl groups in the hydroperoxide derivative, and it is always larger in the 2:1 complexes than in the corresponding 1:1 ones. In addition, the presence of methyl groups produces a shortening of this parameter; thus, the shorter Li—O distance in the 1:1 complexes is obtained for the complex 3:Li$^+$, being 0.021 Å longer in the 2:Li$^+$ complex and 0.026 Å longer in the 1:Li$^+$ complex than in 2:Li$^+$. A similar tendency is observed in the 2:1 complexes. Regarding the comparison between the homo- and heterochiral 2:1 complexes, the Li—O

distance is always slightly shorter in the heterochiral complexes than in the homochiral ones.

The complexation with the lithium cation produces an elongation of the O—O bond of 0.005 Å in the parent compound, while in the methyl substituted ones it is twice as long (0.01 Å).

Table 5. ^1J **Indirect Coupling Constants (Hz) for Each Molecule (1, 2, and 3) and Their Corresponding Complexes Calculated with the SOPPA Method**

	$^1J(O-O)$	$^1J(O-H)$	$^1J(O-Li)$
1	18.13	−60.24	
	$(33.07)^a$	$(-64.38)^a$	
1:Li$^+$	25.75	−75.22	−6.95
1:Li:**1** (D_2)	25.32	−73.08	−6.27
1:Li:**1** (S_4)	25.32	−73.24	−6.30

	$^1J(O-O)$	$^1J(O-H)$	$^1J(O-C)$	$^1J(O-Li)$
2	13.85	−61.97	21.80	
2:Li$^+$	20.05	−73.71	20.35	−7.73
2:Li$^+$:**2** (C_2-A)	18.90	−71.51	20.26	-6.78^b
2:Li$^+$:**2** (C_2-B)	18.96	−71.63	20.29	-6.78^b
2:Li$^+$:**2** (C_1)	18.96	−71.73	20.27	-6.80^b

	$^1J(O-O)$	$^1J(O-C)$	$^1J(O-Li)$
3	24.21	19.64	
	$(6.85)^a$	$(22.06)^a$	
3:Li$^+$	16.50	20.40	−8.25
3:Li$^+$:**3** (D_2)	15.01	20.35	−7.08
3:Li$^+$:**3** (S_4)	c	c	c

^{a} Based on the experimental geometry reported in Table 1. ^{b} Average values. ^{c} The **3**:Li$^+$:**3** (S_4) complex was not calculated due to triplet instabilities.

Something similar happens with the O−C distances, where the bond increases up to 0.03 Å due to the complex formation.

Optical Rotatory Power. Among the experimental measurement of the chirality, the ORP is without any doubt the more important one. Experimental and theoretical reports have shown the importance of the environment and molecular association on the value of this property.[46−49] The calculated ORP values of the isolated molecules and the calculated complexes have been gathered in Table 3. The calculated ORP values of **1** provide similar values using the experimental and calculated geometries. In contrast, the values of **3** are very different due to problems of the computational method used to reproduce the experimental dihedral angle.

Complexation with the lithium cation to form the 1:1 complexes reduces the ORP with respect to the isolated molecule in cases **1** and **2**, while **3**, which does not show ORP when isolated (planar conformation), presents a large value when complexed to Li$^+$. The evolution of the 2:1 complexes follows the same trend as the 1:1 in the cases of **1** and **3** while the opposite tendency is observed for complex **2**. Interestingly, the 2:1 complex of **1** changes its sign with respect to the isolated monomer **1**. The values of the XOOX′ dihedral angles along with the studied complexes are independent of the ORP values for a given molecule or for clusters of different molecules.

Chemical Shieldings. The absolute chemical shieldings of the systems considered are reported in Table 4. The calculations provide similar values when the experimental and calculated geometries of **1** and **3** are used, as they have the largest differences in the chemical shielding of the oxygen atoms.

The complexation with the lithium cation produces an important shift at higher fields of the oxygen atoms signals except for the OCH$_3$ moiety of the **2**:Li$^+$ complex, for which the shift occurs toward lower fields. The effect is smaller in the OH

Scheme 2. Racemization Pathways of the Isolated XOOX′ Molecules
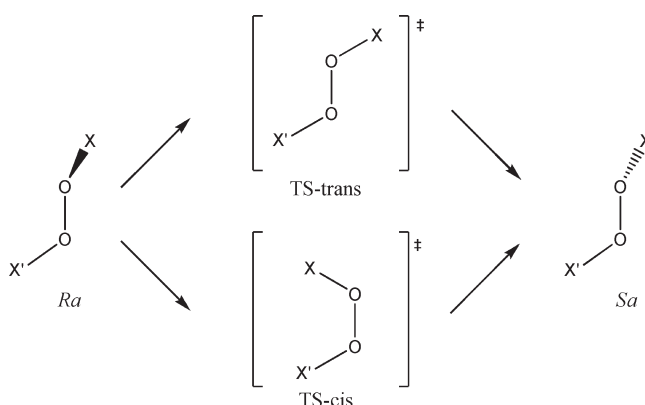
Table 6. Racemizacion Barriers (kJ mol^{-1}) Calculated at the MP2/6-31+G(d,p) Computational Level

	isolated			1:1 complexes			2:1 complexes		
TS conf.	1	2	3	1	2	3	1	2	3
cis	31.2	24.9	47.3	29.6	23.1	31.8	34.2	28.5	39.5
trans	4.6	1.2	0.0	50.9	52.4^a	45.1	47.3	46.7^a	40.3
trans-2					46.4^b			42.2^b	

^{a} The OH moiety is closer to the Li than the OCH$_3$ one. ^{b} The OCH$_3$ moiety is closer to the Li than the OH one.

groups, where the variation is between 4 and 6 ppm, than in the OCH$_3$ ones. The signals of the atoms directly attached to the oxygens shift to lower field, the larger variation being −2.1 ppm among the hydrogen atoms and −7.5 ppm for the carbon ones. The effect observed in the 2:1 complexes is similar to that observed for the 1:1 complexes but less marked.

Small differences are observed between the chemical shielding of the homo- and heterochiral dimers, the larger difference being 0.26 ppm between the oxygen atoms of the **3**:Li$^+$:**3** complexes.

Indirect Coupling Constants. The calculated ^1J coupling constants are presented in Table 5. Intermolecular couplings at two or more bonds show very small values (<0.005 Hz), and they are not reported. The calculated O−O couplings are very sensitive to the geometry used; thus, important differences are found between the values obtained for the optimized and experimental geometries.

For the series of compounds **1** and **2** the complexation with Li cation produces a marked increase, in absolute value, of the O−O couplings in approximately 7.6 Hz for **1** and 6.2 Hz for **2**, and all O−H couplings around 15.0 Hz for **1** and 11.7 Hz for **2**. However, the O−C coupling constants in compound **2** decrease with lithiation around 1.5 Hz. Compound **3** shows the opposite behavior for the complexation with Li$^+$; hence $^1J(O-O)$ decrease around 7.7 Hz and $^1J(O-C)$ increase around 0.8 Hz. Therefore, the variation on O−H coupling with lithiation is twice the variation on O−O coupling, which in turn is 10 times larger than the variation on O−C coupling.

Small differences are found between the homo- and heterochiral complexes, the larger difference being 0.1 Hz in $^1J(O-H)$ for the **1** and **2** complexes.

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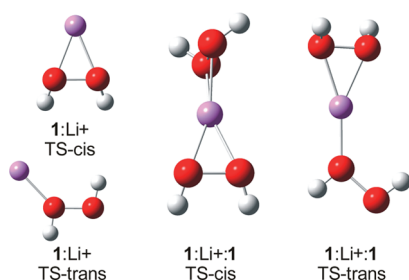
Figure 2. Geometry of the TS structures of the complexes of **1** with the lithium cation calculated at the MP2/6-31+G(d,p) computational level.

Racemizacion Processes. Two possible paths have been described for the isomerization of the hydrogen peroxide derivatives (Scheme 2), and a similar scheme can be proposed for the 1:1 and 2:1 complexes. However, in the case of the two *trans*-TS complexes, differences have been found for paths of molecule **2** due to the different nature of the X and X′ entities. The barriers obtained for the isolated systems (Table 6) are in agreement with previous reports that have shown the *trans*-TS, in general, to be more favorable than the *cis*-TS.[47] This picture completely changes in the 1:1 and 2:1 complexes where the *cis*-TS is more stable than *trans*-TS. In fact, the 1:1 and 2:1 *cis*-TS barriers show values similar to those observed for the corresponding isolated molecules. In contrast, the *trans*-TS barrier increases from a few kJ mol^{-1} in the isolated molecules to about 50 kJ mol^{-1} in the lithium complexes. It is interesting to notice that the *cis*-TS barriers are always larger in the 2:1 complexes than in the corresponding 1:1 ones while the opposite happens with the *trans*-TS ones.

The geometry of the TS structures (Figure 2) shows that while in the *cis*-TS, the lithium cation plays a secondary role; it becomes very important in the *trans*-TS because one of the X groups directly interacts with the lithium atom, significantly increasing the barrier.

■ CONCLUSIONS

A theoretical study of the 1:1 and 2:1 complexes formed by hydrogen peroxide derivatives with the lithium cation has been carried out by means of MP2 computational methods for XOOX′ molecules (**1** X = X′ = H, **2** X = H and X′ = CH$_3$, and **3** X = X′ = CH$_3$). In all cases, the heterochiral complex is more stable than the homochiral one by less than 1 kJ mol^{-1}. The ORP values depend strongly on the lithiation process and on the number of OCH$_3$ entities present in each system. The NMR shielding and ^1J depend more on lithiation than in complexation stereochemistry. This effect on ^1J seems to be more related to the geometrical reorganization of the complexes than to the presence of the Li$^+$ cation.

The NMR values are able to differentiate between the 1:1 and 1:2 stereochemistry of the complexes but not between the homo- and heterochiral complexes.

The *cis*-TS is the preferred path for the racemization processes in the 1:1 and 2:1 lithium complexes, in contrast with the preferred *trans*-TS observed for the isolated monomers.

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