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## THEORETICAL STUDY OF SOME STRUCTURES OF TITANIUM(IV) COMPLEXES DERIVED FROM 2-, 3- AND 4-HYDROXYL-BENZOIC ACIDS

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**ABSTRACT.** Complexes of fluoride titanium(IV) using hydroxyl benzoic acids as ligands are known for their great interest for care of the teeth, of the oral cavity or of dentures. Their activity is closely linked to the stability of their geometry. In this paper, we studied the structures of Ti(IV) complexes derived from hydroxyl-2-benzoic acid, hydroxyl-3-benzoic and hydroxyl-4-benzoic acids by molecular modelling. Calculations by molecular mechanics, Extended Huckel Theory (EHT) calculations have enabled access to the values of steric energy, bond lengths and bond angles, torsion angles, charges, coordinates of the atoms and the total energy values. The data obtained using molecular modelling are in the same range of those obtained in literature. Both data showed an octahedral structure around the metal ion of Ti(IV) complex with a small distortion.

**KEY WORDS:** Hydroxy benzoic acids, Ti(IV) complexes, Molecular modelling, Steric Energy, Stability

### INTRODUCTION

With the continuous development of computer tools (computers and software), the application of molecular modeling has become indispensable for the structural study of different chemical compounds. Its application in inorganic chemistry has been widely used and allowed to avoid the structural study by DRX analysis which requires obtaining inorganic complexes as single crystals. With its success in coordination chemistry, molecular mechanics has become an important tool in this area [1-6]. Most of molecular mechanics calculations are applied to determinate steric energy of the compounds. The charges, the coordinates of the atoms are calculated using Extended Huckel Theory (EHT). This method proposed by Hofmann [7] and modified by Anderson [8] and then reformulated by Calzaféri [9], has been widely used as a semi-empirical method [10, 11].

Ti(IV) complexes are widely known for their use in catalysis [12, 13], for their biological activity [14, 15] and their use for care of teeth [16]. In this article, we are interested by Ti(IV) fluoride complexes derived from hydroxy benzoic acids, synthesized and characterized by Finidori [16] for their high activity for care of the teeth, of the oral cavity or of dentures. Since the biological and the pharmacological activities of a molecule is strongly linked to the stability of its geometry, we studied the structure of these complexes using molecular modeling ion order to determinate the most stable conformation.

### EXPERIMENTAL

#### *Complex*

The complexes studied in this paper, were synthesized by Finidori [16]. They could be obtained by mixing solid titanium fluoride with a benzoic acid solution in acetonitrile under nitrogen atmosphere.

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The formulas of the titanium(IV) complexes proposed by Finidori [16] are as follows: (i)  $[\text{TiF}_2(\text{hydroxy-2-benzoic acid})_2]$ , (ii)  $[\text{TiF}_2(\text{hydroxy-3-benzoic acid})_2]$ , and (iii)  $[\text{TiF}_2(\text{hydroxy-4-benzoic acid})_2]$ .

#### Method of calculation

To optimize the geometry of these complexes and minimize their energies using Hyperchem (Hypercube Inc. Canada) as software, molecular mechanics calculations were performed using the algorithm of Fletcher Revees [17, 18], with the MM+ force field. Bond lengths and bond angles were calculated by molecular mechanics method while semi-empirical calculations using Extended Huckel Theory (EHT) gave coordinates and charges of the different atoms.

## RESULTS AND DISCUSSION

#### Molecular mechanics calculations

The most stable conformations of the different complexes of Ti(IV) are shown in Figures 1-3, with their steric energies and residual gradients.

The titanium(IV) complexes derived from hydroxy benzoic acids have an octahedral structure. This is in a good agreement with the results found in literature [16, 19, 20]. Steric energies calculated for all complexes, appear higher than those obtained by Lin [21] for the complexes of Fe(III). This difference is probably due to high values of van der Waals energies. Electrostatic energy is negligible.

Bond angles and bond lengths, determined for these complexes, are listed in the Tables 1-6. The Ti-F and Ti-O bond lengths, obtained by calculation, are in the same range with crystallographic data [22] and literature [23]. The bond lengths and bond angles values are different from those of a regular octahedral so this allows us to suggest a distorted octahedral geometry around the metal ion.

Table 1. Some bond lengths for the complex of Ti(IV) derived from the hydroxy-2-benzoic acid.

Atoms	Bond lengths (Å)	Atoms	Bond lengths (Å)
Ti(1)-O <sub>ax</sub> (2)	1.942 [23]	Ti(1)-O <sub>ax</sub> (5)	1.944[23]
Ti(1)-O <sub>eq</sub> (3)	1.943 [23]	Ti(1)-F <sub>eq</sub> (6)	2.046 [22]
Ti(1)-O <sub>eq</sub> (4)	1.944[23]	Ti(1)-F <sub>eq</sub> (7)	2.046 [22]

Table 2. Some bond angles for the complex of Ti(IV) derived from the hydroxy-2-benzoic acid.

Atoms	Bond angles (degrees)	Atoms	Bond angles (degrees)
O <sub>ax</sub> (2)-Ti(1)-O <sub>eq</sub> (3)	89.339	O <sub>eq</sub> (4)-Ti(1)-F <sub>eq</sub> (6)	88.911
O <sub>ax</sub> (2)-Ti(1)-O(4)	91.954	O <sub>eq</sub> (4)-Ti(1)-F <sub>eq</sub> (7)	176.043
O <sub>ax</sub> (2)-Ti(1)-O <sub>ax</sub> (5)	178.162	O <sub>ax</sub> (5)-Ti(1)-F <sub>eq</sub> (6)	89.657
O <sub>ax</sub> (2)-Ti(1)-F <sub>eq</sub> (6)	89.421	O <sub>ax</sub> (5)-Ti(1)-F <sub>eq</sub> (7)	89.154
O <sub>ax</sub> (2)-Ti(1)-F <sub>eq</sub> (7)	89.213	F <sub>eq</sub> (6)-Ti(1)-F <sub>eq</sub> (7)	87.319
O <sub>eq</sub> (3)-Ti(1)-O <sub>eq</sub> (4)	95.002	Ti(1)-O <sub>eq</sub> (2)-C(25)	121.307
O <sub>eq</sub> (3)-Ti(1)-O <sub>ax</sub> (5)	91.471	C(11)-O <sub>eq</sub> (4)-Ti(1)	125.701
O <sub>eq</sub> (3)-Ti(1)-F <sub>eq</sub> (6)	175.93	Ti(1)-O <sub>eq</sub> (3)-C(10)	120.923
O <sub>eq</sub> (3)-Ti(1)-F <sub>eq</sub> (7)	88.790	C(8)-O <sub>ax</sub> (5)-Ti(1)	120.359
O <sub>eq</sub> (4)-Ti(1)-O <sub>ax</sub> (5)	89.618		

Table 3. Some bond lengths for the complex of Ti(IV) derived from the hydroxy-3-benzoic acid.

Atoms	Bond lengths (Å)	Atoms	Bond lengths (Å)
Ti(1)-O <sub>eq</sub> (2)	1.983 [23]	Ti(1)-O <sub>ax</sub> (5)	1.973 [23]
Ti(1)-O <sub>eq</sub> (3)	1.979 [23]	Ti(1)-F <sub>ax</sub> (6)	2.052 [22]
Ti(1)-O <sub>eq</sub> (4)	1.976[23]	Ti(1)-F <sub>eq</sub> (7)	2.051 [22]

Table 4. Some bond angles for the complex of Ti(IV) derived from the hydroxy-3-benzoic acid.

Atoms	Bond angles (degrees)	Atoms	Bond angles (degrees)
O <sub>eq</sub> (2)-Ti(1)-O <sub>eq</sub> (3)	152.560	O <sub>eq</sub> (4)-Ti(1)-F <sub>ax</sub> (6)	89.454
O <sub>eq</sub> (2)-Ti(1)-O <sub>eq</sub> (4)	81.113	O <sub>eq</sub> (4)-Ti(1)-F(7)	162.587
O <sub>eq</sub> (2)-Ti(1)-O <sub>ax</sub> (5)	117.428	O <sub>eq</sub> (5)-Ti(1)-F <sub>ax</sub> (6)	164.224
O <sub>eq</sub> (2)-Ti(1)-F <sub>ax</sub> (6)	77.458	O <sub>ax</sub> (5)-Ti(1)-F <sub>eq</sub> (7)	90.950
O <sub>eq</sub> (2)-Ti(1)-F <sub>eq</sub> (7)	81.491	F <sub>ax</sub> (6)-Ti(1)-F <sub>eq</sub> (7)	86.019
O <sub>eq</sub> (3)-Ti(1)-O <sub>eq</sub> (4)	117.560	C(11)-O <sub>ax</sub> (5)-Ti(1)	114.637
O <sub>eq</sub> (3)-Ti(1)-O <sub>ax</sub> (5)	81.672	Ti(1)-O <sub>eq</sub> (3)-C(24)	114.797
O <sub>eq</sub> (3)-Ti(1)-F <sub>ax</sub> (6)	82.551	Ti(1)-O <sub>eq</sub> (2)-C(8)	127.932
O <sub>eq</sub> (3)-Ti(1)-F <sub>eq</sub> (7)	78.525	C(21)-O <sub>eq</sub> (4)-Ti(1)	127.832
O <sub>eq</sub> (4)-Ti(1)-O <sub>ax</sub> (5)	97.740		

Table 5. Some bond lengths for the complex of Ti(IV) derived from the hydroxy-4-benzoic acid.

Atoms	Bond lengths (Å)	Atoms	Bond lengths (Å)
Ti(1)-F <sub>eq</sub> (2)	2.046 [22]	Ti(1)-F <sub>ax</sub> (5)	2.046[22]
Ti(1)-O <sub>eq</sub> (3)	1.986 [23]	Ti(1)-O <sub>eq</sub> (6)	1.949[23]
Ti(1)-O <sub>ax</sub> (4)	1.986 [23]	Ti(1)-O <sub>eq</sub> (7)	1.949 [23]

Table 6. Some bond angles for the complex of Ti(IV) derived from the hydroxy-4-benzoic acid.

Atoms	Bond angles (degrees)	Atoms	Bond angles (degrees)
F <sub>eq</sub> (2)-Ti(1)-O <sub>eq</sub> (3)	170.723	O <sub>ax</sub> (4)-Ti(1)-O <sub>eq</sub> (6)	84.626
F <sub>eq</sub> (2)-Ti(1)-O <sub>ax</sub> (4)	88.896	O <sub>ax</sub> (4)-Ti(1)-O <sub>eq</sub> (7)	83.528
F <sub>eq</sub> (2)-Ti(1)-F <sub>ax</sub> (5)	93.712	F <sub>ax</sub> (5)-Ti(1)-O <sub>eq</sub> (6)	86.109
F <sub>eq</sub> (2)-Ti(1)-O <sub>eq</sub> (6)	105.537	F <sub>ax</sub> (5)-Ti(1)-O <sub>eq</sub> (7)	105.505
F <sub>eq</sub> (2)-Ti(1)-O <sub>eq</sub> (7)	86.113	O <sub>eq</sub> (6)-Ti(1)-O <sub>eq</sub> (7)	163.202
O <sub>eq</sub> (3)-Ti(1)-O <sub>ax</sub> (4)	89.870	Ti(1)-O <sub>eq</sub> (3)-C(14)	118.836
O <sub>eq</sub> (3)-Ti(1)-F <sub>ax</sub> (5)	88.955	C(8)-O <sub>eq</sub> (7)-Ti(1)	128.935
O <sub>eq</sub> (3)-Ti(1)-O <sub>eq</sub> (6)	83.492	Ti(1)-O <sub>ax</sub> (4)-C(24)	118.832
O <sub>eq</sub> (3)-Ti(1)-O <sub>eq</sub> (7)	84.612	C(20)-O <sub>eq</sub> (6)-Ti(1)	128.923
O <sub>ax</sub> (4)-Ti(1)-F <sub>ax</sub> (5)	170.734		

### Study of complexes geometry

#### Study of the geometry of Ti(IV) complex derived from hydroxy-2-benzoic acid (L<sub>1</sub>)

The most stable conformation of the complex [TiF<sub>2</sub>(hydroxy-2-benzoic acid)<sub>2</sub>] (Figure 1) shows that the ligand is bidentate. It is linked to the central metal by the oxygen of carboxyl and the oxygen of hydroxyl. The oxygen atom O(2) of hydroxyl of the first ligand and the atom O(5) of carboxyl of the second ligand are in axial positions, whereas, the two atoms F(6), F(7) and oxygen O(4) of carboxyl of the first ligand and the atom O(3) of the second hydroxyl occupy the equatorial positions.

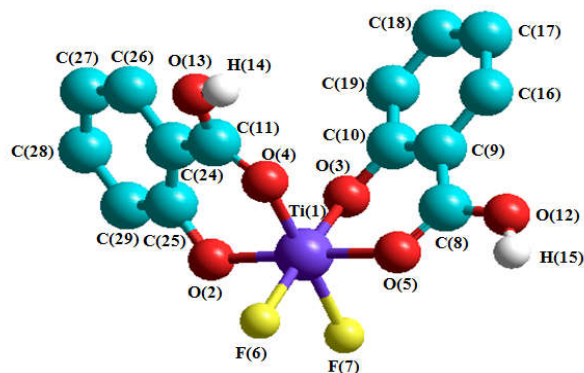


Figure 1. The most stable configuration of  $[\text{TiF}_2(\text{L}_1)_2]$ ; ( $\text{L}_1$ : hydroxy-2-benzoic acid), drawn by Hyperchem. Steric energy: 18.552166 kcal/mol, residual gradient:  $0.007801 \text{ kcal/mol} \cdot \text{\AA}^1$ .

*Study of the geometry of Ti(IV) complex derived from hydroxy-3-benzoic acid ( $\text{L}_2$ )*

The most stable geometry of the complex  $[\text{TiF}_2(\text{hydroxy-3-benzoic acid})_2]$  (Figure 2) indicates that the ligand is bidentate. It is linked to the central metal by the oxygen of carboxyl and the oxygen of hydroxyl, with two fluorine in cis position. The study of this structure (Figure 2) shows that F(6) and the oxygen atom O(5) of the hydroxyl occupy the axial positions. While the two carboxylic oxygen atoms O(2), O(4) of both ligands and F(7), O(3) are in equatorial positions.

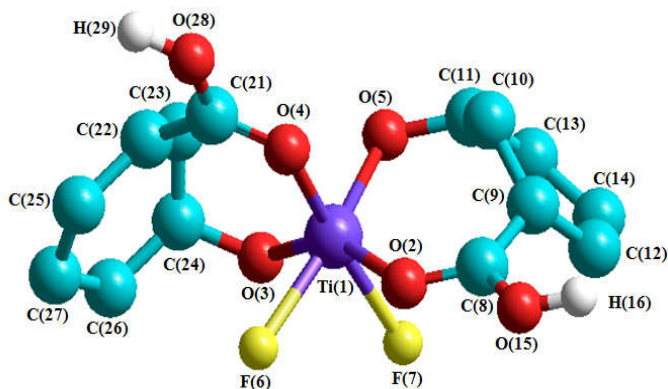


Figure 2. The Most stable configuration of  $[\text{TiF}_2(\text{L}_2)_2]$ ; ( $\text{L}_2$ : hydroxy-3-benzoic acid), drawn by Hyperchem. Steric Energy: 112.927994 kcal/mol, residual gradient:  $0.007703 \text{ kcal/mol} \cdot \text{\AA}^1$ .

*Study of the geometry of Ti(IV) complex derived from hydroxy-4-benzoic acid (L<sub>3</sub>)*

The most stable conformation of the complex [TiF<sub>2</sub>(hydroxy-4-benzoic acid)<sub>2</sub>] (Figure 3) shows that the ligand is bidentate, it is bonded to the central metal by the oxygen of carboxyl and the oxygen the hydroxyl.

F(5) and the oxygen atom O(4) occupy the axial positions. The two oxygen atoms O(6), O(7), F(2) and O(3) are in equatorial positions. The two fluorine atoms are in the cis position.

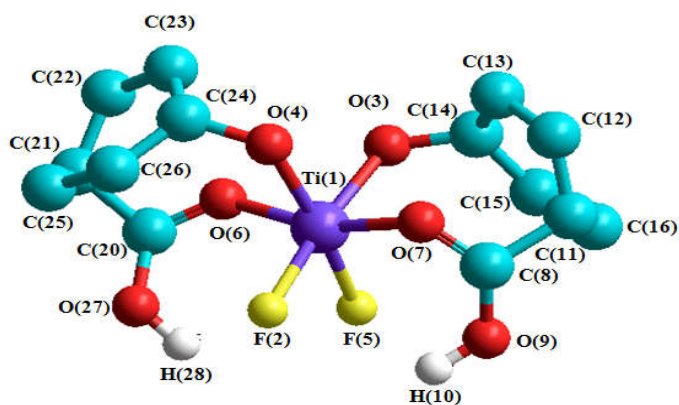


Figure 3. The most stable configuration of [TiF<sub>2</sub>(L<sub>3</sub>)<sub>2</sub>]; (L<sub>3</sub>: hydroxy-4-benzoic acid), drawn by Hyperchem. Steric energy: 216.058548 kcal/mol, residual gradient: 0.007380 kcal/mol<sup>-1</sup>.Å<sup>1</sup>.

*Semi-empirical calculations*

In Table 7, we reported charges and coordinates (calculated by Extended Huckel Theory (EHT)) of the complexes atoms. The charges are small and agree with those reported in literature [24]. They show an insignificant electrostatic contribution.

Table7. Charges and coordinates of the atoms in complexes.

Atom	Z	Charge	Coordinates (Angström)		
			X	y	Z
[TiF <sub>2</sub> (hydroxy-2-benzoic acid) <sub>2</sub> ]					
1	22	3.614	-0.703	-0.510	1.967
2	8	-1.210	-2.390	-0.868	1.073
3	8	-1.211	0.240	-1.215	0.422
4	8	-1.017	-0.690	1.332	1.347
5	8	-1.016	0.969	-0.193	2.906
6	9	-0.930	-1.736	0.096	3.626
7	9	-0.930	-0.748	-2.401	2.748
[TiF <sub>2</sub> (hydroxy-3-benzoic acid) <sub>2</sub> ]					
1	22	3.847	-0.152	0.098	0.182
2	8	-1.022	0.860	0.837	1.720
3	8	-1.224	-1.229	-1.309	-0.701
4	8	-1.020	-0.863	1.941	0.161
5	8	-1.219	0.726	0.132	-1.585

6	9	-0.934	-1.377	-0.336	1.770
7	9	-0.934	0.883	-1.596	0.709
[TiF <sub>2</sub> (hydroxy-4-benzoic acid) <sub>2</sub> ]					
1	22	3.830	0.311	0.127	0.026
2	9	-0.931	1.699	1.591	0.365
3	8	-1.235	-1.066	-1.163	-0.595
4	8	-1.235	-1.118	1.432	0.470
5	9	-0.931	1.716	-1.352	-0.138
6	8	-1.015	-0.088	-0.629	1.777
7	8	-1.015	0.142	0.885	-1.761

### CONCLUSION

The theoretical study of the complex plays an important role in the description of the stereochemistry of these compounds. The theoretical results are in fact considered as a complement to the experimental results. Calculations by molecular mechanics allowed to determinate the most stable geometry for Ti (IV) complexes derived from hydroxy benzoic acids. The data obtained by molecular mechanics calculations and extended Huckel Theory (EHT) fall into the same range with those found in literature and crystallographic data. This approach by molecular modeling is successful because it allowed us to find the same data of crystallographic analysis. These calculations indicate that the [TiF<sub>2</sub>(2-hydroxyl-benzoic acids)<sub>2</sub>] is strongly stabilized compared to the other complexes studied. This study suggests the existence of an octahedral structure for the Ti(IV) complexes derived from 2-, 3- and 4- hydroxyl-benzoic acids. Calculations have shown that these structures have less distortion.

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