Journal of Chemical, Biological and Physical Sciences

An International Peer Review E-3 Journal of Sciences

Available online at www.jcbsc.org

Section A: Chemical Sciences

CODEN (USA): JCBPAT Research Article

Theoretical Approach of the Binary Complexation of Hg(II) with 2,4-D, MCPA and MCPP

Habiba ELJAZOULI [1], Mohamed LAABD [1] and Abdallah ALBOURINE [1*]

[1]Laboratory of Materials and Environment (LME), Department of Chemistry, Faculty of Sciences, Ibn Zohr University, BP 8106, Agadir, Morocco.

Received: 25 November 2014; **Revised:** 9 December 2014; **Accepted:** 23 December 2014

Abstract: The experimental study of the binary complexation of phenoxy-acetic acids 2,4-D (2,4-dichlorophenoxyacetic acid), MCPA (Chloro-MethylPhenoxy acetic acid) and MCPP (Chloro-MethylPhenoxy-Propionic Acid) with mercuric ion Hg(II) has been completed by the characterization of the different ligands using a quantum computation system based on a semi-empirical method Austin Model 1 (AM1) . This review covers electronic, structural and energy aspects. We found that a more stable complexes are those with two ligands : $L_2Hg(H_2O)_2$, $L_2Hg(OH)_2$ and $L_2Hg(OH)(H_2O)$ (LH : 2,4-D ; MCPA ; MCPP) and on the other hand the donor effect of substituent R in α of carboxyl group increases the stability of the complexes in passing from 2,4–D towards MCPA and MCPP and thereafter the chelating power of these ligands vis-à-vis the Hg (II) ion obeys , in agreement with the experiment, with the following order : **MCPP > MCPA > 2,4-D**

Furthermore, the rigidity of the formed coordinate-covalent bond (formerly known as the dative bond, now obsolete) : metal-ligand moving in the same direction as that of the capacity of the three herbicides complexed Hg(II) and consequently they are complexes formed with MCPP which are more difficult to degrade and eventually more harmfull to the environment.

Key words: Herbicides, Phenoxy-acetic acids, Binary complexation, Hg(II) ion, AM1.

INTRODUCTION

Herbicides have harmful properties, because of their acute toxicity[1-3], to aquatic systems not only in the state of isolated ligands [4-7] but especially when they are able to complex heavy metals[8-12]. In fact, this may induce the formation of stable complexes which then alter the properties of the herbicide and its mobility. Evaluate the ability of herbicides to form complexes with metals therefore seems essential. It is in this context that we are interested in further work, in the physicochemical study of their complexes in aqueous solution with heavy metals such as mercury (II) and cadmium (II)[13]. This study was carried out by potentiometric measurements.

To complete this work on the complexation by a theoretical study, it is necessary to characterize the different ligands by a quantum calculation using the semi-empirical method AM1 well suited to the molecules and to complexes of large sizes like in our case.

This method developed by Dewar *et al.* group[14]. Found also various applications in both the of basic and applied research fields. This procedure is established in the programs AMPAC and MOPAC[15]; proved to be considerably effective. The introduction of a pseudo-diagonalization to the SCF (Self Consistent Field) iterations[16] and the accuracy of results make this method widely used in many fields of chemistry. Also it is a very reliable method for the calculation of enthalpies of formation[14, 17-19].

Our study will allow the determination of molecular structures, enthalpies of formation in the series studied. The theoretical results are compared with experimental data[13].

RESULTS AND DISCUSION

Determining energetic, structural and electronic parameters of each molecule is carried out using the algorithm Davidon-Fletcher-Powell[20] with AM1 by using the RHF (Restricted Hartree-Fock) Version of the program MOPAC, version 6.0 with the keyword *''PRECISE''*.

Atomic Charges: The analysis of the net charges of heteroatoms X (O and Cl) allows identifying the active sites vis-a-vis the metal ion Hg(II). With AM1 net atomic charge Q_X is calculated using the equations (1): $Q_X = z_X - \sum_{p \in X} P_{pp}$ with $P_{pp} = 2 \sum_i C_{ip}^2$

Z is the atomic number of the atom X, P_{pp} is the electronic population of the atomic orbital p and C_{ip} is the coefficient of development LCAO (Linear Combination of Atomic Orbitals).

The different results obtained after optimization of the geometry of each molecule in the neutral and deprotonated state allows for an analysis of net charges of heteroatoms (Figure 1) and labile hydrogen atoms Q_H of the acid function and the interatomic distance LO-H in the table 1.

It appears from the analysis of this table that the hydrogen atom of the acid function of 2,4-D carries the highest positive charge, followed by the 2.4-MCPA and finally that of 2,4-MCPP :

Q (H2,4-D) > Q (HMCPA) > Q (HMCPP)

This leads to the following order of deprotonation: **2,4-D > 2,4-MCPA > 2,4-MCPP**

This result correlates well with on the one hand, with that obtained at the order of L_{O-H} bond:

L_{O-H} (2,4-D) > L_{O-H} (MCPA) > L_{O-H} (MCPP)

And on the other hand, with the experimental results [13] represented by the acidity constant pK_a since it increases from 2.4 D to 2,4-MCPA, and to2,4-MCPP.

Furthermore, at the deprotonated state, the examination of the charges of heteroatoms (Figure 1) reveals significant differences in the atomic charges.

Table 1: Net charges Q_H and interatomic distance L_{O-H} calculated by AM1 method.

Molecule	Q_H	L_{O-H} (Å)	pK_a (exp) [16]
2,4-D	0.246	0.990	2.75
2,4-MCPA	0.244	0.973	3.00
2,4-MCPP	0.242	0.952	3.28

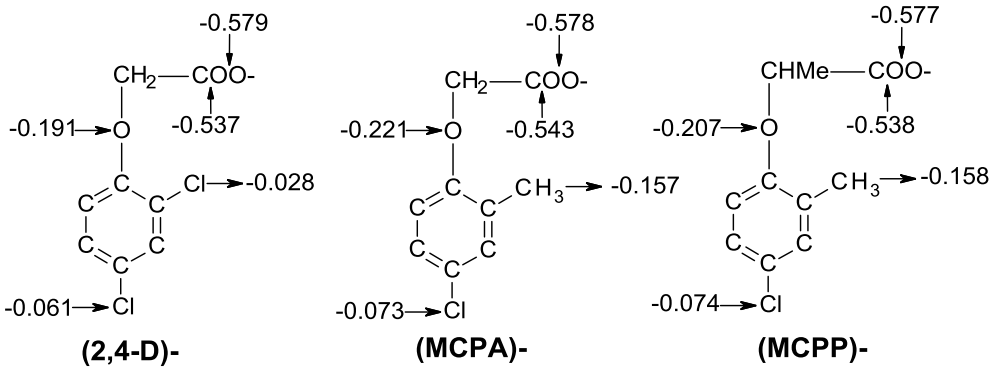

Figure 1: Net charges of heteroatoms of the deprotonated molecules calculated by AM1.

In fact, the oxygen atoms of the acid function present the highest negative charges relative to the chlorine atoms and oxygen in β of the carboxylic group. For the latter, its hydrogen bonding with the hydrogen of the acid function, as shown in figure 2, is likely the cause of the negative charge rating decrease. This indicates therefore a very strong nucleophilic character of the oxygen atoms of the acid; which will grant them a high reactivity with entities such as the positively charged metal ions.

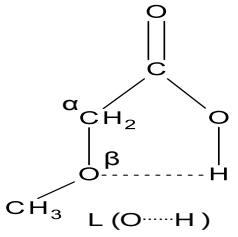

Figure 2: Hydrogen bonding L(O····H) ≈ 2.2 Å.

Complexation by Hg(II): Mercury (II) has a great tendency to form complexes and the coordination number and characteristics stereochemical arrangements are the coordinance numbers two (linear) and four (tetrahedral). Studies of complexation in solution[13], carried out in our laboratory, on these three phenoxyacetic acids with the metal ion mercuric; revealed that the complexes formed are monodentate

and the complexation took place via the oxygen atom of the carboxylic group (according to what is provided with AM1 by analyzing atomic charges) and according to a method which uses the coordination number four of Mercury.

According to this experimental study isolable complexes are of the type HgL, HgL_2, Hg(OH)L, $Hg(OH)L_2$, $Hg(OH)_2L$ and $Hg(OH)_2L_2$. Thus our theory exam was based on the following simple and hydroxylated complexes in which the presence of water molecules can satisfy the coordination number four of mercury (II): $HgL(H_2O)_3$, $HgL_2(H2O)_2$, $Hg(OH)L(H_2O)_2$, $Hg(OH)L_2(H_2O)$, $Hg(OH)_2L_2$ and $Hg(OH)_2L(H_2O)$. (L: 2,4-D; MCPA and MCPP).

a. Stability of the mercuric complexes: On the energy level, the study of the coordination of a metal ion with a ligand L requires the calculation of enthalpies of formation (ΔH_f) that are useful for evaluating the stability of the complexes formed. That is why we determined the ΔH_f's with AM1 (Table 2) of considered mercuric complexes. The examination of values in this table allowed us to derive interesting conclusions that can be summarized as follows:

- The Complexes stability evolves as follows:

$LHg(H_2O)_3 < LHgOH(H_2O)_2 < LHg(OH)_2(H_2O) < L_2Hg(OH)_2 < L_2Hg(H_2O)_2 < L_2HgOH(H_2O)$

This means that the most stable complexes for the three types of acids are $L_2Hg(OH)(H_2O)$. It is therefore: $(2,4\text{-D})_2Hg(OH)(H_2O)$, $(MCPA)_2Hg(OH)(H_2O)$ and $(MCPP)_2Hg(OH)(H_2O)$.

- For the Most stable complexes in accordance with the experiment [13], the substituent donor effect (substitution of a chlorine atom or of hydrogen by a methyl) increases the stability by passing from 2,4-D towards MCPA and MCPP for the complexes $L_2Hg(OH)(H_2O)$ which means that it is the 2,4-MCPP which possesses the most efficient carboxylic function to bind to the mercuric ion. This means that the AM1 method reproduces the effect of substituent complexed state.

Table 2: Enthalpies of formation of the mercuric complexes calculated by AM1.

Ligand (L)	Complexes of the Hg(II)	ΔH_f (kcal/mol)
2,4-D	$(2,4D)Hg(H_2O)_3$	-118.91
	$(2,4D)Hg(OH)(H_2O)_2$	-249.22
	$(2,4D)Hg(OH)_2(H_2O)$	-272.00
	$(2,4D)_2Hg\ (H_2O)_2$	-323.63
	$(2,4D)_2Hg(OH)(H_2O)$	-350.43
	$(2,4D)_2Hg(OH)_2$	-313.83
2,4-MCPA	$(MCPA)Hg(H_2O)_3$	-121.38
	$(MCPA)Hg(OH)(H_2O)_2$	-252.64
	$(MCPA)Hg(OH)_2(H_2O)$	-277.63
	$(MCPA)_2Hg\ (H_2O)_2$	-330.08
	$(MCPA)_2Hg(OH)(H_2O)$	-357.98
	$(MCPA)_2Hg(OH)_2$	-307.61
	$(MCPP)Hg\ (H_2O)_3$	-106.28
	$(MCPP)Hg\ (OH)(H_2O)_2$	-255.88

2,4-MCPP	(MCPP)Hg $(OH)_2(H_2O)$	-284.09
	$(MCPP)_2Hg$ $(H_2O)_2$	-336.08
	$(MCPP)_2Hg$ $(OH)(H_2O)$	-361.15
	$(MCPP)_2Hg$ $(OH)_2$	-311.44

b. Structural analysis: The geometric structures of all studied species, neutral and complexed were fully optimized in their ground state using the AM1 method. In order to examine, with AM1, the mode of complexation of these mercuric species, we proceeded to optimize the geometric structure of the different complexes from the two possible structures, namely the square-planar structure, taking into account the isomers cis and trans, and the tetrahedral structure (Figure 3).

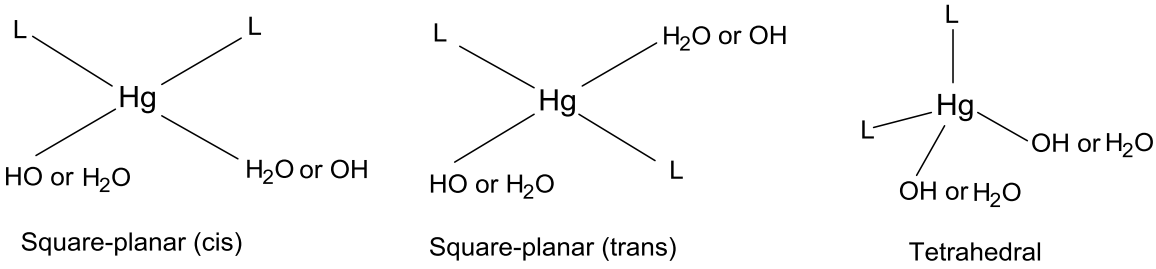

Figure 3: Square-planar and tetrahedral structures of the mercuric complexes (L: 2,4-D; MCPA or MCPP).

After optimization, the geometric parameters of these complexes in square-planar form (cis and trans), moving towards the structure of a distorted tetrahedron. In fact, plane angles α_1, α_2, and α_3 (Figure 4) (Table 3) have variants values between 73° and 124°, and the values of dihedral angles D_1 ($O_2HgL_1O_1$) and D_2 ($L_2HgL_1O_1$) are of about 120°. On the contrary, from a tetrahedral structure, geometrical parameters optimization leads to a less distorted tetrahedral structure and thus more regular since the angles α_1, α_2 and α_3,vary between 109° and 116°, and the angles D_1 and D_2 are of the order of 120° (Table 4).

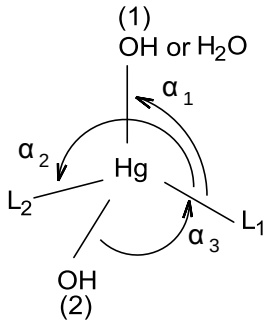

Figure 4: Geometric parameters in the vicinity of the Hg(II) ion complexation sites.

Table 3: Dihedral and planes angles in the vicinity of the Hg(II) complexation sites, from Square-planar structure. D_1 = angle ($O_2HgL_1O_1$) and D_2 = angle ($L_2HgL_1O_1$).

Neutral and complexed species	α_1	α_2	α_3	D_1	D_2
2,4-D	-	-	-	-	-
$(2,4D)_2Hg(H_2O)_2$	115.3	112. 2	114.2	120.3	121.1
$(2,4D)_2Hg(H_1)(H_2O)$	116.1	116.4	110.3	119.4	121.9
MCPA	-	-	-	-	-
$(MCPA)_2Hg(H_2O)_2$	116.9	112.9	113.6	119.9	120.8
$(MCPA)_2Hg(H_1)(H_2O)$	113.4	110. 5	112.8	120.6	121.3
MCPP	-	-	-	-	-
$(MCPP)_2Hg(H_2O)_2$	115.3	109.1	114.1	120.5	121.2
$(MCPP)_2Hg(H_1)H_2O$	116.0	110.3	110.6	121.4	122.7

Table 4: Dihedral and planes angles in the vicinity of the Hg(II) complexation sites from tetrahedral structure. D_1 = angle ($O_2HgL_1O_1$) and D_2 = angle ($L_2HgL_1O_1$).

Neutral and complexed species	α_1	α_2	α_3	D_1	D_2
2,4-D	-	-	-	-	-
$(2,4D)_2Hg(H_2O)_2$	123.4	94. 8	120.6	117.6	121.3
$(2,4D)_2Hg(H_1)(H_2O)$	115.7	115.3	73.6	118.3	122.0
MCPA	-	-	-	-	-
$(MCPA)_2Hg(H_2O)_2$	124.1	106.9	90.5	118.9	122.8
$(MCPA)_2Hg(H_1)(H_2O)$	122.3	73. 8	123.9	119.5	123.5
MCPP	-	-	-	-	-
$(MCPP)_2Hg(H_2O)_2$	-118.2	-101.3	93.9	119.9	123.0
$(MCPP)_2Hg(H_1)(H_2O)$	120.7	115.0	73.2	121.3	123.9

This deformation of the tetrahedron is probably due to the presence of lone pairs of the oxygen atoms around the metal ion, causing repulsions which influence angles αi (Figure 5).

These repulsions are however compensated by hydrogen bonds (Figure 6) between the hydrogen molecule of H_2O and the OH group, with the oxygen of the carboxylic group of the ligand.

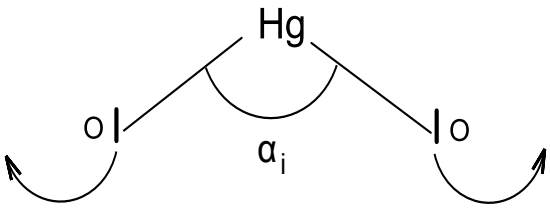

Figure 5: Repulsion of electron lone-pairs of the oxygen atoms.

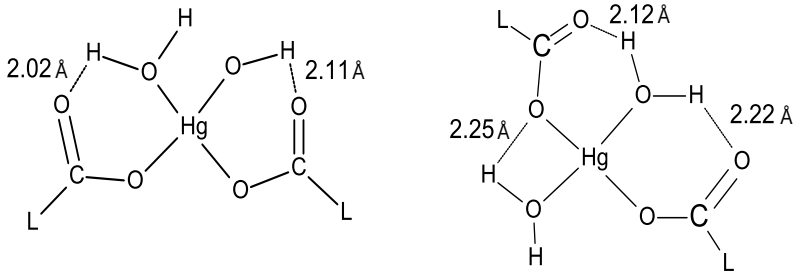

Figure 6: Hydrogen bonds in the tetrahedral complexes.

c. Ligand-metal bond (L-Hg): The complexation of a ligand L results in the formation of a bond between the latter and the metal ion M. The nature of this connection continues to be an interesting point of research. With this in mind we will look with AM1 the order of this bond and its effects on the geometric structure of the different ligands that form coordinate covalent bonds by intervening with a free electron pair of the oxygen atom vis-a-vis Hg (II) possessing vacant atomic orbitals in its valence shell: $6s^0 6p^0$ (Figure 7).

The formation of this bond causes the reorganization of the electron cloud and therefore a geometric rearrangement of the molecular system especially in the immediate vicinity of the active site. And when we know that the energy variation due to the geometric the reorganization constitutes a significant part of the total energy of the system, it is necessary to optimize the structural parameters of the complexes formed.

The geometrical parameters optimized with AM1, corresponding to the vicinity of the site of complexation (Figure 8) are reported in tables 4 and 5 for the mercuric complexes.

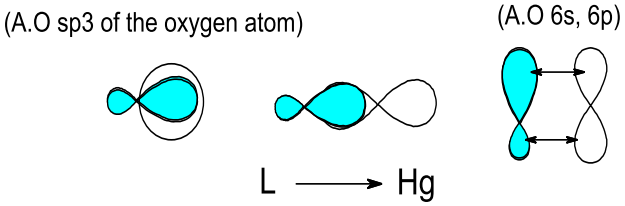

Figure 7: Coordinate covalent bond resulting from overlapping between A.O valence of the oxygen atom (of L) and Hg(II).

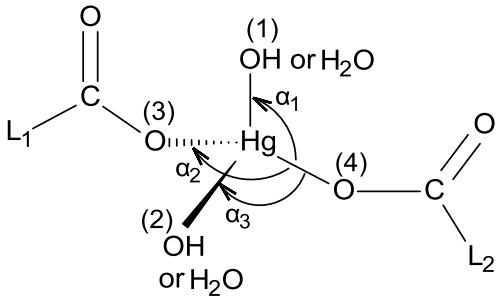

Figure 8: Geometric parameters in the vicinity of the Hg(II) ion complexation sites.

The values of these parameters show that going from the O-H bond of the acid to the O-M complex bond, there is an extension that reaches 1.39 Å in the mercuric complexes. This is because the radius of the mercuric ion ($r_{Hg(II)}$ = 1.1 Å) is larger than the radius of the hydrogen atom which it replaces (r_H = 0.53 Å). Furthermore, the length of the Hg-O bonds (varying between 2.22 Å and 2.36 Å) depending on the substituent, shows that this bond is rigid.

Table 5: Bond lengths (Å) in the vicinity of the Hg(II) complexation sites.

Neutral and complexed species	O-H	L (O-M) (Å)				C=O	C-OH	C-OM
		$M-OL_1$	$M-(OH)_1$	$M-OL_2$	$M-(OH)_2$			
2,4-D	0. 990	-	-	-	-	1. 233	1. 355	-
$(2,4D)_2Hg(H_2O)_2$	-	2. 271	2. 276	2. 268	2. 273	1. 891	-	1. 282
$(2,4D)_2Hg(H\text{-}1)(H_2O)$	-	2. 241	2. 120	2.310	2. 294	1. 254	-	1. 288
MCPA	0.973	-	-	-	-	1. 234	1.355	-
$MCPA)_2Hg(H_2O)_2$	-	2. 270	2. 276	2. 364	2. 374	1. 291	-	1. 282
$(MCPA)_2Hg(H\text{-}_1)(H_2O)$	-	2. 258	2. 147	2. 359	2. 341	1. 285	-	1. 277
MCPP	0. 952	-	-	-	-	1. 234	1. 358	-
$(MCPP)_2Hg(H_2O)_2$	-	2. 271	2. 277	2. 261	2. 276	1. 288	-	1.284
$(MCPP)_2Hg(H\text{-}_1)(H_2O)$	-	2. 218	2. 134	2. 297	2. 294	1. 283	-	1.283

We also note that going from C-OH to C-OM, the C-O bond undergoes a shortening that reaches 0.067 Å. This reflects that under the effect of the complexation, this bond becomes more rigid (Table 5). This confirms that the degradation of complexed species is more difficult than those of the neutral species.

It therefore follows that the AM1 method is quite reliable to give a qualitative description of the geometric structures of these compounds.

REFERENCES

1. M. Raveton, P. Ravanel, M. Kadouji, M. Tissut, Actes du 2ème congrès du groupe Français des pesticides, Bordeaux; 1994, 89.
2. L. C. Folmar, H. O. Sanders, A.M. Julin, Archives of Environmental Contamination and Toxicology; 1979, 8 (3), 269.
3. J. P. Salaun, Actes du 2ème congrès du groupe Français des pesticides, Bordeaux: 1994, 208.
4. G. Martin, Tech et doc, Lavoisier publication; 1979, Paris 12.
5. R. E. Green, C. C. K Liu, N. Tamrakar, Amer. Chem. Soc. Symposium series; 1986, 315, 366.
6. J. Salessy, Revue de l'agence de l'eau Adour-garonne, 1990.
7. F. Matsumura, G. Mallory Boosh, T. Misato, Academic press, NewYork, San Fransisco, London, 1972.
8. M. Cruz-Guzmán, R. Celis, M. C. Hermosin, J. Cornejo, R. Hance, Environmental Science & Technology; 2004, 38(1), 180.
9. R. Hance, Canadian Journal of Soil Science; 1969, 49, 357.

10. S. U. Khan, Canadian Journal of Soil Science; 1974, 54, 235.
11. P. Jamet, M. A. Piedallu, Phytiatrice-Phytopharmacie; 1975, 24, 279.
12. O. Fadayomi, G. F. Warren, Weed Science; 1977, 25, 97.
13. N. Mounir, H. El Jazouli, M. El Amine, F. Masbouh, H. Kabli, Y. Ait Ichou, A. Albourine, Chemical Speciation and Bioavailability; 2007, 19, 45
14. M. J. S. Dewar, D. M. Storch, Journal of the American Chemical Society; 1985, 107, 3898.
15. M. J. S. Dewar, E. G. Zoebisch, E. F. Healy, J. J. P. Stewart, Journal of the American Chemical Society; 1985, 3902.
16. J. P. P. Stewar, P. Csaszar, P. Pulay, Journal of Computational Chemistry; 1982, 3, 227.
17. R. Volets, J. P. François, J. M. L. Martin, J. Mullens, J. Yperman, L. C. Van Poucke, Journal of Computational Chemistry; 1989, 10(4), 449.
18. R. Volets, J. P. François, J. M. L. Martin, J. Mullens, J. Yperman, L. C. Van Poucke, Journal of Computational Chemistry; 1990, 11(3), 269.
19. W. J. Welsh, Journal of Computational Chemistry; 1990, 11(5), 644.
20. W. C. Davidson, Chemical Speciation and Bioavailability; 1986, 10, 406.

*** Corresponding author: *A. ALBOURINE***

Department of Chemistry, Faculty of Sciences, Ibn Zohr University, BP 8106, 80000, Agadir, Morocco.

Email: albourine.abdallah@gmail.com