THEORETICAL INVESTIGATION OF INORGANIC COMPLEXES IN SANDWICH FASHION (BONDING MODE AND ELECTRONIC STRUCTURE)

MECHERI Sabri[1*], ZOUCHOUNE Bachir[1,2]

[1] *Laboratoire de chimie appliquée et technologie des Matériaux, Université Larbi Ben M'Hidi – Oum El Bouaghi, 04000 Oum El Bouaghi, Algérie*

[2] *Unité de Recherche de Chimie de l'Environnement et Moléculaire Structurale, Université Constantine (Mentouri Constantine), 25000 Constantine, Algeria*

Code CCO 5

Email* : sabrimecheri0@gmail.com

Introduction & Objectives:

Many bimetallic complexes containing metallic multiple bonds have been synthetized since the discovery of the quadrupole bond between Re(III)-Re(III) [1].

The aim of this study is to investigate the behaviour of the multiple bond in the presence of allylic ligands in the sandwich complexes (Ligand)[(Cl)Fe_2L_2] (Ligand = All^-, Cp^-, Ind^-; L = CO, PEt_3).

Computational details:

Density functional theory (DFT) calculations were carried out using the 2012 version of the Amsterdam Density Functional (ADF) program [2]. The BP86 and the hybrid-type B3LYP* functionals have been used for calculations.

Results and Discussion:

Both the BP86 and B3LYP* showed that all structures prefer the high spin state.

The small HOMO-LUMO gaps in all structures are consistent with the energy differences between the triplet and singlet spin states. However, the M-M bond distance of the singlet structures of the CO group stands in the range of 1.99-2.24 Å, and is slightly affected by the change of auxiliary ligands. Thus are verified by both the WIB and the MBO, which refers to a triple Fe-Fe bond in (All)[(Cl)$Fe_2(L)_2$] structures and a double Fe-Fe bond in [(Cl)Fe(L)]$_2$, (Cp)[(Cl)$Fe_2(L)_2$], and (Ind)[(Cl)$Fe_2(L)_2$] (L = CO, PEt_3).

Conclusion:

In the $(\mu\text{-Cl})^-$ and $(\eta^3\text{-Allyl})^-$ structures each Fe(I) receive 2-electrons vs. 3-electrons from $(\eta^5\text{-Cp})^-$ and $(\eta^5\text{-Ind})^-$ bridging ligands. The electronic structure shows the occupation of the π_2* orbital in the [(Cl)FeL]$_2$, (Cp)[(Cl)Fe_2L_2] and (Ind)[(Cl)Fe_2L_2] complexes (L = CO, PEt_3) which leads to the elongation of the bond length. Whereas, the Fe(1)–Fe(2) correspond to triple bond which agreed by the WIB and MBO in (All)[(Cl)Fe_2L_2] structures.

Keywords: Spin state, ligand.

References

1. Cotton, F. A., Curtis, N. F., Harris, C. B., Johnson, B. F. G., Lippard, S. J., Mague, J. T., ... & Wood, J. S. (1964). Mononuclear and polynuclear chemistry of rhenium (III): its pronounced homophilicity. Science, 145(3638), 1305-1307.

2. ADF2013, S C M (2012) Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands.