

## Conformational analysis, NBO and QTAIM Study of the Antimony Complexes with Mesoionic 1, 3-Thiazolium-5-thiolate

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### INTRODUCTION

In recent years, antimony complexes have been widely studied as antimicrobial agents, anticancer, and precursor of thin films<sup>1</sup>. Mesoionic compounds have attracted interest because of their unusual electronic structure and application in medicine and nonlinear optics. In this work, we calculated molecular conformations, electronic structure, thermodynamic stabilities and chemical bonds properties for  $\text{SbX}_3(\text{L})$  ( $\text{X} = \text{F}, \text{Cl}, \text{Br}$ ;  $\text{L} = \text{C}_{17}\text{H}_{14}\text{NS}_2\text{Cl}$ ) complexes in gas phase. Our objective was to get a detailed interpretation on the chemical bonds, in special, on the change in the electronic structure of mesoionic ligands after coordination.

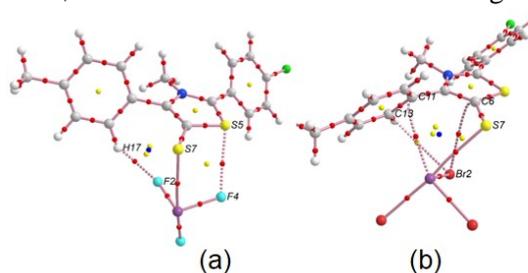
### METHODS

The potential energy curves (PECs) for all complexes were calculated from the 360° rotation around the Sb–S bond, using B3LYP, M06-2X and MP2 level with 6-31G(d) basis set with semi-relativistic pseudopotential (ECP) for Sb. After that, the minimum structures of the PECs were fully optimized and characterized by vibration analysis, using M06-2X/cc-pVTZ level with relativistic ECP for Sb. Besides, the basis set superposition errors were estimated using counterpoise protocol. Chemical bonds were studied by Quantum Theory of Atoms in Molecules (QTAIM)<sup>2</sup>. NBO calculations were performed to compute atomic charges and hybrid natural orbitals. All the calculations were carried out with Gaussian 09 and AIMALL programs.

### RESULTS AND DISCUSSION

The PECs calculated by using MP2 and M06-2X methods were quite similar. Thus, the method M06-2X was selected to study the complexes. The calculated thermodynamic parameters indicated that the formation of the complexes is spontaneous, with  $\Delta G_r$  ranging from -33.43 to -27.27  $\text{kJ}\cdot\text{mol}^{-1}$ . The analysis of NBO charges for the complexes indicated which the metal coordination led to the loss of mesoionic character, producing large charge

delocalization in the ring. The  $s$  character of Sb lone pair ( $\text{Lp}$ ) increase from 83.0% in  $\text{SbF}_3(\text{L})$  to 86.6% in  $\text{SbCl}_3(\text{L})$ , and to 89.1% in  $\text{SbBr}_3(\text{L})$ . Moreover, the NBO  $\text{Lp}$  orbital energies of the Sb change from -13.53eV [in  $\text{SbF}_3(\text{L})$ ] to -15.37eV [in  $\text{SbBr}_3(\text{L})$ ], indicating a greater stability for  $\text{SbBr}_3(\text{L})$  lone pair electrons. Using the results from QTAIM, we were able to classify the Sb–S bonds as closed shell, with small degree of electrons sharing. Also, the intramolecular interactions in the complexes were classified by QTAIM into three types: i) hydrogen bonds, ii) halogen bonds and iii)  $\text{Sb}-\pi$ , as is shown in the following figure.



**Figure 1.** QTAIM path and bond critical points (in red) for: (a)  $\text{SbF}_3(\text{L})$  and (b)  $\text{SbBr}_3(\text{L})$ .

### CONCLUSIONS

Our study showed that the ground state geometries for all  $\text{SbX}_3(\text{L})$  complex are stabilized by non-covalent interactions such as hydrogen bonds, halogen bonds, and  $\text{Sb}-\pi$  and  $\text{Sb}-\text{S}$  interactions. In addition, the NBO analysis indicated that the metal coordination produce a greater charge delocalization in the mesoionic ring, resulting in a larger stability.

### ACKNOWLEDGMENT

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<sup>1</sup> I. I.Ozturk and C.N. Banti, J. Inorg. Biochem., 109, 57, (2012).

<sup>2</sup> F. C. Cortés, R. F.W. Bader. Coord. Chem. Rev., 246, 633, (2005).

<sup>3</sup> A. Schlzu, A. Villinger, Chem. Eur. J. Chem., 18, 2902,(2012).