Chemical Bonding and Electronic Configuration of Nitrosyl Iron Complexes

I-Jui Hsu[a], Tze-Yuan Wang[a], Jey-Jau Lee[a], Chung-Hung Hsieh[b], Gene-Hsiang Lee[a], Wen-Feng Liaw[b], Yu Wang[a], [a]*National Taiwan University, Taipei, Taiwan.* [b]*National Tsing Hua University, Hsinchu, Taiwan*. E-mail: ijuihsu@yahoo.com

The nitrosyl non-heme iron complexes with sulfur ligands are extensively synthesized to study the interaction of NO and iron-sulfur protein. In this report, the electron density distribution of mono- and di-nitrosyl iron sulfur compounds are studied with multipole model based on X-ray diffraction data. In the dinitrosyl iron complexes (DNIC), the coordination sphere of Fe is a tetrahedral $Fe(NO)_2(S)_2$ core such as $[S_5Fe(NO)_2]^-$ and $[Fe(NO)_2(SR)_2]^{-1/0}$. In five-coordinated complexes, it turns out to be a tetragonal pyramidal $Fe(NO)(S)_4$ geometry for mononitrosyl complexes such as $[(NO)Fe(S, S\text{-}C_6H_4)_2]^{-1/-2}$and $Fe_3(NO)_3(S, S\text{-}C_6H_4)_3$. To illustrate the bonding character, the topological properties associated with the bond critical points (BCP), Laplacian of the electron density as well as electron density at the BCP of each chemical bond will be presented. The comparison between experiment and theory will be made. Because of the ambiguity of the traditional way to discriminate the oxidation states of NO, NO^+ and NO^- group by bond angles and vibrational frequency, the X-ray absorption spectroscopy of Fe K-, L-edge and N/O/S K-edge are used to investigate the oxidation state of metal, NO groups and sulfur lignads. Moreover, the magnetic susceptibility and electron paramagnetic resonance results will be included to illustrate the electronic configuration among Fe and NO groups. Based on the Enemark-Feltham notation, all results toward the conclusion that the best way to describe the present dinitrosyl and mononitrosyl cases are $\{Fe^{+1}(\bullet NO)_2\}^9$ and $\{Fe^{+1}(NO^{+1})\}^7$.

Keywords: nitrosyl, BCP, x-ray absorption spectroscopy