

# Theoretical Studies on the Electronic Structures and Spectroscopic Properties of a Series of Dioxoosmium (VI) Complex

L.Y. Liu<sup>(1)</sup>, Y. H. Zhang<sup>(1)</sup>, J. Z. Qiao<sup>(2)</sup>, C. A. Taft<sup>(1)\*</sup>,

(1) Centro Brasileiro de pesquisas Físicas, Rua Dr.Xavier Sigaud, 150,22290 Rio de Janeiro, Rio de Janeiro, Brazil.

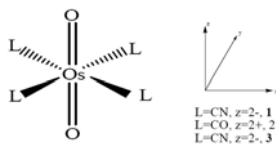
(2) The Second senior high school of Changchun , ChangChun 130023, China

**Abstract** – The electronic structures and spectroscopic properties of a series of *trans*-dioxoosmium complex ions  $[\text{Os}(\text{VI})\text{O}_2(\text{L})_4]^{2-}$  (L = CN, z = 2- (1); L = CO, z = 2+ (2); L = CCH, z = 2- (3)) were investigated using quantum chemistry method. The geometry structures of the complexes were fully optimized at the B3LYP level for the ground state and the CIS level for the lower-lying excited state with the LANL2DZ basis sets along with two f-type (for Os) and two d-type (for C, N, and O) polarization function, respectively. The calculations revealed that the bond lengths of Os=O in the excited state are elongated relative to those in the ground state for the three complexes. The calculation results show that the dipole-allowed absorptions of the three complexes are in the region of  $\lambda > 230$  nm. The calculated phosphorescence at 617 nm /638 nm and 553 nm originate from  $^3[(\pi^*(\text{Os}=\text{O}))^1(\text{Os}(d_{xy})+\pi(\text{CN}/\text{CCH}))^1]$  and  $^3[(\pi^*(\text{Os}=\text{O}))^1(p_z(\text{O}))^1]$  excited state for **1/3** and **2**, respectively. The phosphorescence energies are in the order of **2**>**1**>**3**, therefore the emission can be influenced and tuned by the attached ligands.

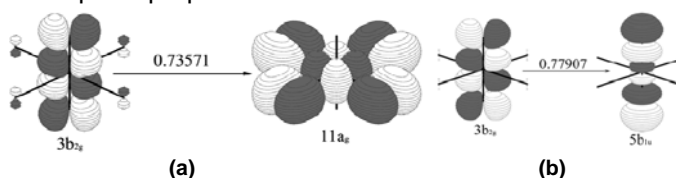
*Trans*-dioxo transition metal complexes have the interesting structural, spectroscopic, photochemical, and electrochemical properties, and can be used as materials of catalysts and reagents for oxidation reactions [1]. For example, *trans*-dioxo complexes of Mo, Mn, Cr, Ru, and Os are quite well-known catalyzer for the stoichiometric oxidation reactions of organic substrates. To these dioxo transition metal complexes, ones identically believed that the active centers as a powerful oxidant are mainly concentrated on the  $\text{MO}_2$  segment, which can induce photochemical or electrochemical reaction, therefore excited extensively to investigation experimentally and theoretically on this type of complex.

For the complex  $[\text{OsO}_2(\text{CN})_4]^{2-}$ , in experiment, Preetz and coworkers [2] have observed absorption and emission spectrum of the solid tetramethyl-ammonium salt at 10 K, the electronic origin is deduced and verified by characteristic isotopic shifts by  $^{18}\text{O}$  and  $^{13}\text{C}$ , and concluded Os=O bond length elongation 10-13 pm in excited state via Frank-Condon theory. At the same time, Che et. al [3] found  $[\text{Ph}_4\text{As}]_2[\text{OsO}_2(\text{CN})_4]$  emit at 700 nm in MeCN at room temperature and the Os-O band is weakened in the  $^3E_g$  excited state. The rich optical properties of  $[\text{OsO}_2(\text{CN})_4]^{2-}$  has attracted the attention of theorists. Hummel et. al [4] have studied the geometry structures of  $[\text{OsO}_2(\text{CN})_4]^{2-}$  employing DFT method. For the complex  $[\text{OsO}_2(\text{CO})_4]^{2+}$ , Bernhardt et al [5] attempted experimentally to obtain  $[\text{OsO}_2(\text{CO})_4][\text{Sb}_2\text{F}_{11}]_2$ , however, they are failed in purifying the product. The  $-\text{C}\equiv\text{CH}$  which is isoelectronic to  $\text{C}\equiv\text{O}$  and  $\text{C}\equiv\text{N}$ , and also typical  $\pi$ -bonding ligand, However, up to now, no reports on complex  $[\text{OsO}_2(\text{C}\equiv\text{CH})_4]^{2-}$ .

In this work, the geometry and electronic structures of the three *trans*-dioxo Osmium (VI) complexes in the ground and excited states together with their photophysical properties are theoretically explored. The elongated Os=O bond indicates that it is more possible for the Os=O bond to suffer broken in the excited state. This is favorable as the photo-catalyst and photo-reaction reagent. The calculated lower-lying absorptions and luminescence for the complex **1** and **3** with the  $-\text{C}\equiv\text{N}$  and  $-\text{C}\equiv\text{CH}$  ligands arise from the metal-centered d-d transition but assisted by the ligand to acquire the transition intensity. Compared to **1** and **3**, the stronger  $\pi$ -accepting CO ligand in **2** leads to the dipole-allowed lower-lying excited state, consequently the blue-shifted phosphorescence. Conclusively, the  $\pi$ -acidity ligands ligated to the dioxo-osmium block affect their electronic structures and optical properties.



**Fig. 1.** The geometry structure of the complexes.



**Fig. 2.** The single electron transition for the emission at 617 nm of **1** (a) and 553 nm of **2** (b) under the TD-DFT calculation.

[1] Stewart, R In "Oxidation in Organic Chemistry", Part A and Part B, Wiberg, K. B., New York, 1962, pp1-227

[2] Sartori, C.; Preetz, W. Z. Naturforsch. 1988. 43a. 239.

[3] Che, C.-M.; Yam, V. W.-W.; Cho, K.-C.; Gray, H. B. Chem. Commun.1987. 948.

[4] Hummel, P., Winkler, J. R.; Gray, H. B. Dalton Trans. 2006, 168