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The Electronic Structure of Molecular Ion $[Mo(qdt)_3]^{2-}$ (qdp: quinoxaline-2,3-dithiolate)

Wen LI*, Jian Ping YE, Chen Ho TUNG

Institute of Photographic Chemistry, The Chinese Academy of Sciences, Beijing 100101

Abstract: The electronic structure of the molecular ion has been calculated by DV-Xα method. The calculated nitrogen atomic charge is high in negative. The frontier molecular orbitals are mainly composed of Mo and S atomic valence orbitals. Total density of state reveals that there are wide bands below and above the E_f energy.

Keywords: Molybdoenzymes, electronic structure, quantum chemistry.

Researchers had found that molybdoenzymes are of crucial importance in a number of human physiological and pathological contexts. Up to now, at least 30 molybdoenzymes have been found[1]. Most of these enzymes contain Moco (the molybdenum cofactor) which consists of a pterin-ene-ditholate organic ligand (molybdopterin) and a single Mo atom. Hence, the enzymes and model systems have received growing attention.

The title molecular ion is one of the model examples. Some authors reported that the coupled proton electron transfer relevant to Moco could be observed in its reaction[2,3]. Therefore, in order to establish the relationship between its structure and property we calculated the electronic structure of the molecular ion $[Mo(qdt)_3]^{2-}$ by DV-Xα method[4]. The geometry was taken from the molecular structure analyzed by four-circle X-ray diffraction[5]. The ion with D_{3h} symmetry was shown in **Figure 1**. Nine kinds of atoms were classified due to different atom or chemical environment— Mo, S, C1, N, C2, C3, C4, H1(-C3) and H2(-C4). The calculated atomic orbitals are: $Mo4s^14d^55s$, $S3s^23p^43d$, $N2s^2\,2p^3$, $C2s^22p^2$ and $H1s^12s$. The other inner AOs were frozen. α parameter was 0.7, and Wattson sphere model was adopted for the ion (R=20Å and Q=2). The convergent factor is 1×10^{-5}.

Some important results are given below. The calculated bond orders are 0.386 (Mo-S), 0.596 (C1-S), 1.047 (N-C1), 0.822 (N-C2), 0.884 (C2-C3), 1.00 (C4-C3), 0.801 (C3-H1), and 0.637 (C4-H2). From the bond orders, Mo-S bond is far weaker than S-C1, so it is not the general rings such like C_6H_6, pyridine, *etc*. In the five-membered ring MoS_2C_2, there is not strong delocalized MOs. Hence, it is not necessary that the ligand and Mo atom must be coplanar. In fact, usually the ligand $C_8N_2S_2$ plane is folded with respect to the MoS_2 plane.

Figure 1. The geometry of molecular Ion $[Mo(qdt)_3]^{2-}$

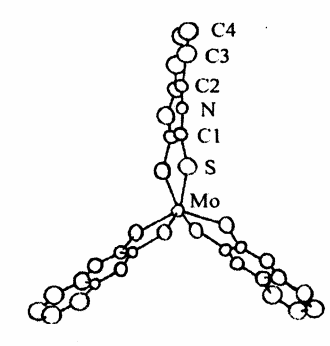
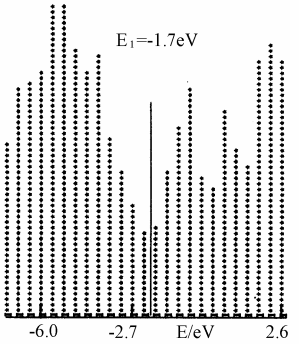


Figure.2. Total density of state for MOs



The calculated atomic charges:1.418 Mo, -0.300 S, 0.074 C1, -0.333 N, 0.178C2, -0.328 C3, -0.122 C4, 0.178 H1, and 0.084 H2. Nitrogen atom has the most negative charge; C3 and S also have more negative charges. So, when it presents in acidity solution, H^+ readily combines with nitrogen atom of the ligand. This is in accord with the experimental protonation phenomenon [2]. The total density of state for MOs is shown in **Figure 2**. The atomic valence orbital composition of some frontier molecular orbitals is shown in **Table 1**. The frontier molecular orbitals not only imply that Mo atom could play an active center in the reaction of the ion but also the detailed analysis of its electronic structure could provide the deep understanding for the catalyzing mechanism of Moco.

Table 1. The compositions of some frontier molecular ion orbitals

MO No.	-E(eV)	Composition	Character
87(E#)	3.6601	0.02Mo+0.69S+0.15N+0.14C	
88(A_2#)	3.5070	0.01Mo+0.91S+0.01N+0.06C	
89(A_1#)	3.0246	0.66S+0.04C1+0.12N+0.19C	
90(A_2')	2.7831	0.61S+0.01C1+0.21N+0.17C	
91(A_1')	2.0652	0.59Mo+0.25S+0.07C1+0.07N+0.02C	HOMO
92(E')	1.3110	0.14Mo+0.07S+0.13C1+0.23N+0.43C	LUMO

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