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论文

咪唑桥连双核铜SOD模拟物的电子结构及催化活性的理论研究

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## 摘要：

利用半经验PM3和密度泛函B3LYP方法研究了 $\beta$ -环糊精咪唑桥连双核铜SOD模拟物( $\{[\text{Cu}(\text{L})\cdot(\text{H}_2\text{O})(\beta\text{-CD})]\}_2(\text{im})\}^{3+}$ )、模拟物的衍生物及模拟物与底物分子结合的复合物分子的电子结构，运用自然键轨道(NBO)方法对该体系的电荷分布及成键特征进行了分析。计算结果表明，该模拟物中核心Cu离子与配体 $\text{H}_2\text{O}$ 分子的结合较弱，在进行超氧阴离子自由基催化反应中可被其它配体所取代。胍基的存在使得超氧化物歧化酶中Cu所带的正电荷增多，而有利于催化反应的进行。与其它配位原子相比，与两个五元环连接的N原子与Cu配位能力相对下降，这也将有利于提高Cu离子与底物的结合能力。由于自由基分子形式，使得超氧化物歧化酶模拟物与反应底物( $\text{O}_2^-$ )在酸性条件下结合后的络合物中五重态构型比相应的单重态构型更加稳定。同时双核之间的咪唑桥环也对稳定该模拟物的构型起到了一定的作用。

关键词： MP3和DFT/B3LYP方法 SOD模拟物 自然键轨道理论 脯基

## Theoretical Studies on Electronic Structures and Catalytic Activities of Superoxide Dismutase Mimetics of Imidazolate-bridged Dinuclear Cu(II) Complexes

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### Abstract:

Electronic properties of superoxide dismutase(SOD) mimetics, the water-insoluble imidazolate-bridged dinuclear Cu(II) complex,  $\{[\text{Cu}(\text{L})(\text{H}_2\text{O})(\beta\text{-CD})]_2(\text{im})\}^{3+}$ , where L is 4-(4'-*tert*-butyl)benzyl-diethylenetriamine,  $\beta$ -CD is  $\beta$ -cyclodextrin and im is imidazolate, and its guanidinium-containing derivatives were studied with semi-expire PM3 and *ab initio* DFT/B3LYP methods. The analysis of charge distribution and bond characters for all studied systems were performed by using the Natural Bond Orbital(NBO) theory. The present calculated results show that the combination of the central Cu ion in the complex with water molecule is weak. It is possibly occurred that the water molecule is substituted by the superoxide radical anion in the catalytic reaction.  $\beta$ -Cyclodextrin linked to the guanidine causes more positive charge localizing at the central Cu cation of  $\{[\text{Cu}(\text{L})(\text{H}_2\text{O})(\beta\text{-GCD})]_2(\text{im})\}^{3+}$ , which is favorable to catalyze the dismutation reaction. The combination of Cu ion in the complexes with the ligand N atom linked to two pentagons is much weaker than other ligands N atoms around the central Cu ion of these complexes. The structures of spin quintuplet state of  $\{[\text{Cu}(\text{L})(\text{OOH})(\beta\text{-CD})]_2(\text{im})\}^{3+}$  and  $\{[\text{Cu}(\text{L})(\text{OOH})(\beta\text{-GCD})]_2(\text{im})\}^{5+}$  are more stable than those of spin singlet states of these complexes. Additionally, the imidazolate-bridge localized at the middle of two central Cu ions in these complexes is helpful to stabilize these mimetic complexes.

Keywords: MP3 and DFT/B3LYP method SOD mimetics NBO theory Guanidines

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