

## 叠氮酸桥联双核铜配合物磁耦合的密度泛函研究

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收稿日期 修回日期 网络版发布日期 接受日期

**摘要** 在密度泛函理论的框架下,采用对称性破损态方法,对EE,EO两种连接方式叠氮酸桥联双核铜模型配合物进行计算,结果表明,EE方式连接为反铁磁耦合;EO方式则为铁磁耦合,但只发生在 $\theta=91^\circ\sim 107^\circ$ 区间,与实验值 $96^\circ\sim 104^\circ$ 基本一致,研究揭示了其磁耦合构效关系的本质在于SOMO b<sub>1g</sub>轨道中N $\mu$ 的P<sub>x</sub>轨道与Cu的d<sub>xy</sub>轨道间的d-p-d三中心 $\sigma$ 反键作用,在 $\theta=91^\circ\sim 110^\circ$ 区间具有最大的反键重叠,因而铁磁耦合最大,同时发现J值随Cu与配位叠氮酸N原子间距离的增大而减小,但叠氮酸偏离平面的角度对J值影响不大。

**关键词** [叠氮酸](#) [桥键](#) [对称性](#) [破损](#) [双核配合物](#) [叠氮络合物](#) [铁磁材料](#) [铜络合物](#) [构效关系](#)  
[密度函数](#)

分类号 [0641](#)

## Ab initio calculation for magnetostructural characterization of azido-bridged Cu(II) dimers

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**Abstract** On basis of the broken symmetry approach and density functional theory (DFT), the magnetostructural characterization of azido-bridged c Cu(II) dimers is studied which have end - to - end (EE) and end - on (EO) two main coordination modes. The calculating results show that EE mode gives antiferromagnetic interaction, whereas EO mode gives ferromagnetic coupling in which  $\theta$  is about  $91^\circ\sim 107^\circ$ , basically agree with the experimental value  $96^\circ\sim 104^\circ$ . The essence of the magnetostructural characterization lies in d - p - d three centers  $\sigma$  antibonding action between two Cu d<sub>xy</sub> orbitals and bridged N p<sub>x</sub> orbital in SOMO b<sub>1g</sub>. In the  $\theta$  region of  $95^\circ\sim 110^\circ$  the  $\sigma$  antibonding overlap has the maximum, which leads to the maximum ferromagnetic coupling. It is also shown that  $\tau$  has no great influence on J, whereas J decreases linearly with increasing r<sub>Cu-N $\mu$</sub> .

**Key words** [BRIDGE BOND](#) [SYMMETRY FAILURE](#) [DINUCLEAR COMPLEX](#) [AZIDO COMPLEX](#) [FERROMAGNETIC MATERIALS](#) [COPPER COMPLEX](#) [STRUCTURE ACTIVITY RELATIONSHIP](#)

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