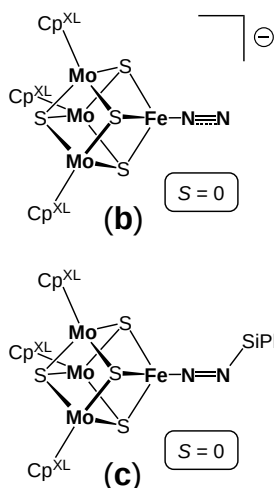


酵素模倣型[Mo₃S₄Fe]クラスター錯体による N₂ 還元反応の理論計算
N₂-Reduction catalyzed by Biomimetic [Mo₃S₄Fe] Clusters: A Computational Study

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研究成果概要

The development of transition metal clusters for catalytic N₂-reduction is an active area of inorganic chemistry. The electronic structure of the transition metal clusters and its relations to the catalytic activity can be rationalized from quantum chemical methods, most commonly employing density functional theory (DFT).



In this study, we have calculated the electronic structures of the N₂-bound [Mo₃S₄Fe] clusters; [$\{Cp^*_3Mo_3S_4Fe\}_2(\mu-N_2)]^{2-}$ (**a**), [$Cp^{XL}_3Mo_3S_4Fe(N_2)]^-$ ($Cp^R = Cp^{XL}$ (**b**), and [$Cp^{XL}_3Mo_3S_4Fe(N_2SiPh_3)]$ (**c**). Geometries of the possible spin states of **a**, **b**, and **c** were optimized using DFT and standard basis sets. According to DFT calculations, the ground state of **a**, **b**, and **c** is $S = 0$. Structural parameters of the optimized ground state structures are in agreement with the X-ray structures. Electronic structure analysis indicated that the oxidation state of Fe in all three systems is Fe(II) but slightly reduced.

発表論文(謝辞あり)

(*) W. M. C. Sameera, Y. Takeda, Y. Ohki, “Transition metal catalyzed cross-coupling and nitrogen reduction reactions: lessons from computational studies”, *Advances in Organometallic Chemistry*, **2022**, 78, in press.

(*) Y. Ohki, K. Munakata, R. Hara, M. Kachi, K. Uchida, M. Tada, R. E. Cramer, W. M. C. Sameera, T. Takayama, Y. Sakai, S. Kuriyama, Y. Nishibayashi, K. Tanifuji, “Nitrogen reduction by the Fe sites of synthetic [Mo₃S₄Fe] cubes”, 12 May 2021, PREPRINT (Version 1) available at Research Square <https://doi.org/10.21203/rs.3.rs-477541/v1>