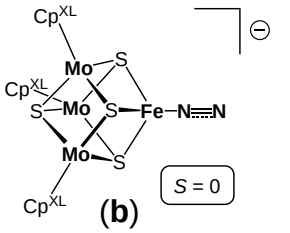
酵素模倣型[Mo_3S_4Fe]クラスター錯体による N_2 還元反応の理論計算
N_2-Reduction catalyzed by Biomimetic [Mo_3S_4Fe] Clusters: A Computational Study

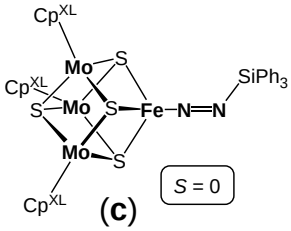
北海道大学　低温科学研究所　　W. M. C. Sameera

研究成果概要

The development of transition metal clusters for catalytic N_2-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).



(**b**)



(**c**)

In this study, we have calculated the electronic structures of the N_2-bound [Mo_3S_4Fe] clusters; [{$Cp^*_3Mo_3S_4Fe$}$_2$(μ-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 [Mo_3S_4Fe] cubes”, 12 May 2021, PREPRINT (Version 1) available at Research Square https://doi.org/10.21203/rs.3.rs-477541/v1