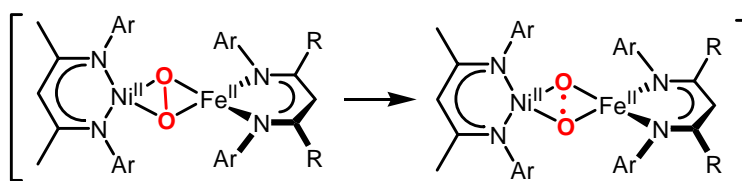
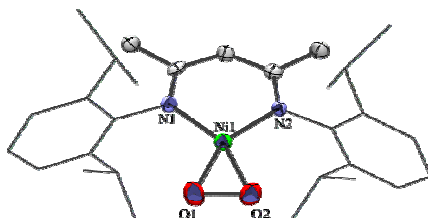


Dioxygenase-Like Activity of an Isolable Ni-Superoxo complex and Monooxygenase-Like Activity of Ni-Heterobimetallic Systems

Yao, S., Berlin/D, Company, A., Berlin/D, Herwig, C., Berlin/D, Limberg, C., Berlin/D, Driess, M. Technische Universität Berlin, Institute of Chemistry, Straße des 17. Juni 135, Sekr. C2, D-10623 Berlin

The chemistry of dioxygen activation by metal complexes is of great importance for understanding the peculiar reaction mechanisms of dioxygen activating metalloproteins in biological systems and utilizing metal complexes as oxidation catalysts. While the bioinspired investigation concerning Fe- and Cu-mediated dioxygen activation has led to numerous stoichiometric and catalytic transformations of organic substrates, the chemistry of non-iron and non-copper systems remains largely unexplored. We are particularly interested in the role of nickel sites, the light congener of extensively used palladium and platinum systems in dioxygen activation and subsequent oxygenation processes. Herein we present the first molecular nickel(II)-superoxo complex LNiO_2 isolable at room temperature,^[1] which performs H-atom abstraction from O-H and N-H bonds and shows an unprecedented dioxygenase-like activity.^[2] Moreover, LNiO_2 proves to be a promising building block for the synthesis of homo and heterobimetallic complexes with a NiO_2M core (M = K, Zn, Ni, and Fe),^[3,4] which display a diverse reactivity including a unique monooxygenase-like activity in the case of the NiO_2Fe compound.



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