

Special Colloquium

TU Berlin, Division of Organic Chemistry in collaboration with UniCat

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Lecturer: **Prof. Dr. Mu Hyun Baik,**
Department of Chemistry,
Indiana University, Bloomington, USA

Title: **Redox Non-Innocent Ligand in Action:
A Novel Mechanism for Protecting Reactive
Intermediates and Storing Energy for the
Activation of CH₄ and O₂**

Abstract: The electronic structures of the low and high-spin states of the cationic complex [Ni(H)(OH)]⁺ that was previously found by Schwarz *et al.* to be highly reactive towards CH₄ and O₂ were examined. Computational work suggested that the low-spin doublet state D₀ of the Ni^{III}-d⁷ system is significantly lower in energy than its high-spin quartet analogue Q₁. Recent DFT-studies indicated, however, that Q₁ is the reactive species requiring Q₁ to have a sufficiently long life time for undergoing thermal reactions with the small molecule reactants under single collision conditions in the gas phase. These observations raise the question as to why Q₁ does not spontaneously undergo intersystem crossing. Our work based on DFT, coupled-cluster and MCSCF calculations suggests that the hydroxyl ligand behaves as a redox non-innocent ligand and becomes oxidized to formally afford an electronic structure that is consistent with a Ni^{II}-(OH)⁺ species. As a result, the doublet and quartet ground states are not related by a single electron spin flip and the intersystem crossing becomes inhibited, as indicated by unexpectedly small spin-orbit coupling constants. After extensive sampling of the potential energy surfaces, we conclude that there is no direct way of converting Q₁ to the ground state doublet D₀. Alternative multi-step pathways for the Q₁ → D₀ decay involving doublet excited states were also evaluated and found to be energetically not accessible under the experimental conditions. To the best of our knowledge this is the smallest reactive molecule where a redox-non innocent ligand plays a key role for the reactivity profile of a transition metal complex.

Date: **Thursday, 10 September 2009**

Time: **5:15 pm - around 6:45 pm**

Location: **TU Berlin, Institute of Chemistry,
Building C
Straße des 17. Juni 115, 10623 Berlin
room C 243**

Organiser: Prof. Dr. H. Schwarz (TUB)

Coffee and tea will be served thirty minutes prior to the lecture start.
Guests are cordially invited to attend!