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学 位 論 文 内 容 の 要 旨

博士の専攻分野の名称 博士（総合化学） 氏名 シェルスター バスティアン
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学 位 論 文 題 名

Theoretical Study on Formation and Reactivity of Coordination Compounds Employing
AFIR
(人工力誘起反応法を用いた配位化合物の生成と反応性に関する理論的研究)

Coordination compounds are a class of functional materials that have attracted immense research efforts over the years due to their enticing properties for a wide range of applications. These include gas storage and separation, catalysis, biological sensing and imaging, drug delivery, and ion exchange, to name some. Herein, two subclasses of coordination compounds are investigated, metal-organic frameworks (MOFs) and transition metal complexes, to address two different, but highly challenging issues.

In the first case, the development of new MOFs is addressed. Targeted synthesis of novel MOFs with desired properties remains highly challenging as their formation mechanisms are poorly understood. Consequently, their discovery is largely driven by chemical intuition and serendipity. In order to realize targeted synthesis of new MOFs based on a solid scientific foundation, rather than empiricism, a deeper understanding of how these structures assemble is paramount.

Therefore, this Thesis aims to contribute to bridging the gap between computational design of hypothetical MOFs and their successful experimental synthesis. A new methodology to address this challenge is presented, and its application to study the early stages of MOF formation is demonstrated.

The second problem addressed concerns the development of new catalysts of industrial importance. Methane has the highest gravimetric energy density of any hydrocarbon, however its handling and storage are difficult due to its low density. As such, a more efficient fuel with greater volumetric energy density can be realized through methane-to-methanol transformation. Nonetheless, no 3d transition metal complexes that can selectively oxidize methane to methanol are currently known. Therefore, the development of catalysts comprising cheap, abundant and non-toxic metals is of immense interest.

The work herein relates the electronic properties of doped cobalt-oxo cubane complexes to their reactive properties, enabling the construction of design principles helpful in the development of new catalysts for methane hydroxylation.

In Chapter 1, an introduction to the work undertaken in this Dissertation is provided. The introduction covers computational chemistry and its development over the past 100 years. The state of the art is described, and challenges that must be overcome to push the field further are discussed. Then, MOFs and their history are reviewed, along with their significance in realizing a sustainable society. Strategies for synthesis and design of new MOFs, as well as their weaknesses, are also addressed, accentuating the necessity for an improved understanding of MOF self-assembly. At last, coordination complexes, being the molecular counterpart to the extended MOF structures, are introduced, and a brief introduction to their applicability as molecular catalysts is given.

Chapter 2 presents the fundamental background of density-functional theory (DFT) and computational elucidation of reaction mechanisms, which in combination lay the theoretical foundation for the work performed herein. The background of DFT, based on the Hohenberg–Kohn theorems, Kohn–Sham DFT and the exchange–correlation problem, is discussed. Thereafter, geometry optimization methods and automated reaction mechanism discovery methods are examined. Particular attention is dedicated to the locally updated planes (LUP) method as well as the artificial force induced reaction (AFIR) method, being two principal tools employed in this Dissertation.

In Chapter 3, a study on the early-stage formation of the SIFSIX-3-Zn MOF is presented. First, the methodology to investigate structural self-assembly, involving the AFIR method, is introduced. Then, its application to the assembly of the SIFSIX-3-Zn MOF node is demonstrated. The structure is shown to assemble in a stepwise fashion, through adduction of one organic ligand at a time. Interconvertibility between intermediates and competing reaction pathways are found, providing a plausible rationale for stochastic multistage processes in MOF formation.

Chapter 4 provides an investigation into the formation of paddlewheel units, and in particular on the effects of axially coordinating ligands and the stability of the resulting structures. Zn-based paddlewheel structures are found to depend strongly on the stabilization of axially coordinating ligands to form a stable structure maintaining a favorable geometry, whereas Cu-based structures are stable also in the absence of axially coordinating ligands. It is shown that the assembly of four of the structures, $[\text{Zn}_2(\text{OAc})_4] \cdot 2 \text{H}_2\text{O}$, $[\text{Zn}_2(\text{OAc})_4] \cdot 2 \text{py}$, $[\text{Cu}_2(\text{OAc})_4]$ and $[\text{Cu}_2(\text{OAc})_4] \cdot 2 \text{H}_2\text{O}$, proceeds through a single phase, in which they assemble directly from their reaction mixtures. $[\text{Cu}_2(\text{OAc})_4] \cdot 2 \text{py}$, on the other hand, is found to form through a two-phase mechanism that first requires the formation of the related $[\text{Cu}_2(\text{OAc})_4] \cdot 2 \text{H}_2\text{O}$ paddlewheel structure. These findings can explain the experimental synthesis procedures.

In Chapter 5, the study on electronic and reactive properties of $[\text{M}(\text{O})\text{Co}_3\text{O}_4(\text{OAc})_4(\text{py})_3]$ ($\text{M} = \text{Cr}, \text{Mn}, \text{Fe}, \text{Mo}, \text{Tc}, \text{Ru}, \text{Rh}$) complexes is presented. Based on its radical character at the terminal oxyl, the reactivity of the Fe analog is investigated in further detail and compared to the experimentally known Ru-doped cubane. The Fe-based structure is found to facilitate methane hydroxylation through the oxygen rebound mechanism, which is shown to be the most favorable reaction the cubane and methane substrate can undergo, supported by AFIR calculations.

At last, in Chapter 6, the Dissertation is concluded. A summary, including the main findings of the Dissertation, is given. It is evident that the self-assembly processes of MOFs, even in the early stages, are non-intuitive and difficult to predict purely based on chemical intuition. In the cubane complexes, a clear relationship between oxyl spin density and catalytic activity has been identified, which may assist the design of novel 3d transition metal-based catalysts of similar structural composition.

An outlook, also discussing possible future directions to advance the field further, is presented. It is clear that there are still challenges that have to be addressed before computational design of new structures can go hand-in-hand with experimental synthesis of novel compounds. Nonetheless, the future of bridging the two areas of computational and experimental chemistry looks bright.