Bis(alkyl-imidazolyl)propionate (BAIP) based bio-inspired mono-nuclear non-heme iron(II) complexes that catalyze challenging oxidative transformations of organic compounds

Sprawozdania

Informacje na temat projektu

BAIPFeOTC

Identyfikator umowy o grant: 657765

Finansowanie w ramach H2020-EU.1.3.2.

Całkowity budżet € 165 598,80

Wkład UE € 165 598,80

Projekt zamknięty

Data rozpoczęcia 1 Września 2015

Data zakończenia 31 Sierpnia 2017

UNIVERSITEIT UTRECHT

Niderlandy

Periodic Reporting for period 1 - BAIPFeOTC (Bis(alkyl-imidazolyl)propionate (BAIP) based bio-inspired mono-nuclear non-heme iron(II) complexes that catalyze challenging oxidative transformations of organic compounds)

Okres sprawozdawczy: 2015-09-01 do 2017-08-31

Podsumowanie kontekstu i ogólnych celów projektu
Mononuclear non-heme iron enzymes featuring a 2-His-1-carboxylate facial triad active site have received particular attention primarily due the stunningly diverse oxidative catalytic transformations that are catalyzed by these enzymes. Many efforts by synthetic inorganic chemists have been devoted to biomimetic modeling studies of the facial triad enzymes in order to understand the immense oxidative power of these enzymes and to develop new synthetic catalysts. Initial studies have focused on the development of functional models of the different subfamilies and employed mostly polydentate all-N donor ligands. While impressive results have been obtained, limited effort has been devoted to the design of models that more faithfully reproduce the coordination environment of the 2-His-1-carboxylate facial triad, i.e. that contain combined N,N,O donor ligands.

In this project, we developed a new class of facial triad N,N,O ligands based on the bis(alkyl-imidazolyl)propionate (BAIP) architecture for the synthesis of bio-inspired mono-nuclear non-heme iron(II) complexes. The reactivities of the synthesized iron complexes towards the oxidative transformation of bio-relevant bidentate substrates have been examined.

Beside that, we have investigated the ligand-based redox chemistry of homoleptic cobalt and zinc complexes derived from a b-diiminate ligand (bis(1-methyl-4,5-diphenyl-1H-imidazol-2-yl)methane anion; an intermediate in the synthesis of the bulky BAIP ligand) that is structurally very similar to widely studied b-diketiminate ligands. These complexes show four reversible/quasi-reversible single-electron oxidations that are all ligand based. The anionic and oxidized pi-radical ligand containing cobalt complexes were synthesized and characterized by a number of spectroscopic and computational techniques that corroborated their ligand-based redox chemistry.

The design and development of highly efficient as well selective catalysts is one of the major goals of research in chemistry. During the last decades, transition metal-catalysed transformations have been dominated by the use of precious metals, for example, Pt, Pd, Rh, and Ir, which are expensive, toxic and scarce. The desire to replace these noble metals by base metals such as iron and cobalt, which are earth-abundant and have no toxicity issues, as catalytic materials represent one on the biggest challenges in the fields of catalysis and synthesis. As part of the general endeavors of creating sustainable chemical production methods, the development and use of catalysts and catalytic reaction procedures is vital. The search for new homogeneous catalysts based on non-noble metals also includes the design of new organic ligands that allow the properties of the catalysts to be tuned and optimized.

Protocols for the design of new sterically encumbered BAIP-ligands for the generation of highly reactive 1:1 Fe/ligand complexes that mimic the bio-inspired mono-nuclear non-heme iron(II) enzymes are the first objective of this project. Next, the physical properties of the resulting iron complexes are an important objective, as these provide insight in the nature of the overall complex and help to correlate their chemical reactivity to their structural design. Another important objective is the study of the chemical reactivity of the iron complexes towards organic substrates. Insight in this reactivity provides a means to link the properties of the iron complexes to those of the non-heme iron enzymes, which they are meant to mimic, and also to investigate their properties as man-made catalysts for important oxidation reactions.
The synthesis of bulky ligands that provide access to iron complexes comprising a single rigid tripodal N,N,O-ligand and readily available coordination sites, thereby leading to a closer mimic of the 2-His-1-carboxylate facial triad found in non-heme iron enzymes, represents the initial part of the proposed research. Accordingly, we have synthesized a di-phenyl substituted bis(alkyl-imidazolyl)propionate (BAIP) ligand where additional phenyl-substituents on the imidazole moieties occupy a significant amount of space in the coordination environment. We have synthesized iron complexes using suitable iron precursor and one equivalent of this ligand resulting in discrete 1:1 complexes. The complexes were characterized by various spectroscopic techniques including single crystal X-ray structure determination. In one typical example, the complex features a 5-fold coordinated iron center, showing that the sterically encumbered facial NNO coordination binding mode using the new bulky BAIP ligand has been achieved. A number of different iron complexes based on the new ligand and containing biorelevant and reactive co-ligands were synthesized next in order to mimic non-heme iron enzymes. We have used sodium phenylpyruvate and o-aminophenol as a co-ligand to mimic α-keto glutarate-dependent enzymes and 2-aminophenol 1,6-dioxygenase, respectively. The outcome of these investigations showed that the ester moiety does not coordinate strong enough to iron in these co-ligand complexes to maintain the N,N,O coordination mode of the ligand. In the next round of investigations, research efforts were therefore focused on the use of the corresponding BAIP carboxylate salt to achieve the N,N,O coordination-binding mode of the ligand. In spite of a plethora of synthesis attempts using various strategies, these efforts lead to the formation of polymeric complexes upon the reaction of the BAIP carboxylate acid salt ligand with a variety of different iron precursors. As a subproject, we have also studied a bidentate N,N ligand which is an intermediate molecule in the synthesis of the bulky BAIP ligand. This N,N ligand framework bears an extended imidazole-based π-system in conjugation with a formal b-diketimine backbone. Bis-ligated cobalt and zinc complexes featuring this anionic ligand have been synthesized and characterized by several spectroscopic techniques including single crystal X-ray analysis. The homoleptic bis-ligated cobalt and zinc complexes were studied by cyclic voltammetry, which showed that these complexes undergo series of four consecutive single-electron oxidations that are all assigned to ligand-based oxidations. The singly and doubly oxidized complexes have been synthesized on a preparative scale and have been fully characterized by various spectroscopic techniques.

**Innowacyjność oraz oczekiwany potencjalny wpływ (w tym dotychczasowe znaczenie społeczno-gospodarcze i szersze implikacje społeczne projektu)**

Beside the proposed investigations of bulky N,N,O ligands based on the BAIP scaffold according to the submitted proposal, the coordination chemistry and ligand-based redox chemistry of the bidentate ligand HBMIMPh2 was also investigated. These investigations have led to some ground-breaking results, which at this stage can be considered as the major scientific accomplishment of the overall project. The redox behaviour of complexes featuring BMIMPh2– or related ligands will be a very versatile tool in contemporary research on metal-ligand radical chemistry, in particular within the context of metal-ligand cooperativity in the domain of chemical catalysis. Ligands like BMIMPh2– may find a wide application scope in, e.g. the activation of small molecules (H2, N2, CO2 etc), in multi-electron reactions as well as electronic applications of molecular systems with multiple accessible redox levels.
Synthesis of non-heme iron enzymes using bulky BAIP ligand to mimic 2-his-1-carboxylate facial triad

Active site of non-heme iron enzymes

Studies of redox non-innocence properties of a diiminate ligand in transition metal complexes

Fe-BAIP complex and Noninnocent b-diiminate ligand

Ostatnia aktualizacja: 16 Stycznia 2018
Numer rekordu: 214959