

Activation of Dinitrogen by Multinuclear Iron and Vanadium Complexes Supported by Linked Sterically Demanding N,N'-subunits

A persistent challenge in chemistry is to activate and functionalize atmospheric dinitrogen molecules. The utilization of abundant N_2 molecules for the synthesis of N-containing valuable products typically requires a prior activation of an N_2 molecule at a redox-active metal center. In biological nitrogen fixation, Nature uses metalloenzyme systems called nitrogenases, among which the most efficient contains a multinuclear molybdenum-iron cofactor, but other systems with iron–vanadium and iron-only cofactors are also known. In industry, ammonia is produced by the Haber–Bosch process under high pressure and elevated temperature conditions where heterogeneous iron or ruthenium catalysts are used in order to convert N_2 and H_2 to NH_3 based. Despite the high efficiency and economy of the Haber–Bosch process, the severe reaction conditions, high energy consumption, and high CO_2 emission are of significant concern to sustainable social development. Hence, both the coordination chemistry of this simple molecule and the search for processes that involve a homogeneous catalyst for the utilization of N_2 as a feedstock to generate higher value organonitrogen materials are continually one of the greatest challenges facing chemists.

Building on the developments in the booming coordination chemistry of dinitrogen and homogenous catalytic systems for dinitrogen functionalization from one side as well as drawing on another hand from our more than a decade of experience in the field of small molecules activation (O_2 , CO_2 , and SO_2) on the main group and transition metal complexes supported by a vast library of organic ligands, in the proposed project we want to use the experience gained in designing reaction systems for fundamental studies of the N_2 activation and transformations mediated by multinuclear iron and vanadium complexes tailored with ligands featuring joined N,N-binding sites of various coordination properties and spatial arrangements. The proposed project is novel in further advancing the fundamental knowledge of the N_2 activation and factors controlling the character and reactivity of the resulting intermediate products by the elaborated redox-active multimetallic cluster/ N_2 reaction systems. While various type of N,N- and N,N,N-ligands have been used extensively in the field owing to their ability to support low-coordinate metal centers that analogous systems involving joined N,N-ligand systems have essentially not been explored until now. Ultimately, project results will provide an in-depth understanding of the rules governing N_2 activation processes involving metal centers, which will be an important step towards the rational design of efficient catalytic systems for industrial applications.