

Abstract

Low-valent Nickel complexes with Sulfur-only and mixed Sulfur and Phosphorus ligand spheres

As nickel complexes with sulfur containing ligands are well known in biological systems, research in the last four decades was mainly focused on the synthesis of nickel thiolate complexes in the oxidation state +II. In the literature there is less information on the selective synthesis of low-valent nickel thiolate complexes. We suppose this to be erroneous, particularly because many low-valent nickel thiolate complexes show exceptional bonding properties. The nickel complexes synthesized and characterized in this thesis give an excellent example of these remarkable properties and they are supposed to be important with reference to metalloenzymes.

The synthesis and characterization of *tert*-thiolate ligands as well as organic sulfides is the focus of the first part of this thesis. In the second part the coordination properties of these ligands towards nickel are investigated. In the framework of the investigation of the reactivity of the *tert*-thiolate ligand with the Ni(II)- or phosphane-Ni(II)-precursor, respectively, new types of two-, five-, fourteen- and twenty-nuclear low valent nickel thiolate complexes with unusual trigonal planar coordination and in some cases additional tetrahedral coordination of the nickel centers were synthesized and structurally characterized. In addition, the new complexes and already described nickel thiolate complexes^[67] $[\text{Ni}_7(\mu_7\text{-S})(\mu\text{-S}t\text{Bu})_8][\text{BzEt}_3\text{N}]$ (**25**), $[\text{Ni}_7(\mu_7\text{-S})(\mu\text{-S}t\text{Bu})_9]_2[\text{Ni}_7(\mu_7\text{-S})(\mu\text{-S}t\text{Bu})_8][(\text{Ph}_3\text{P})_2\text{N}]_3$ (**26**), $[\text{Ni}_8(\mu_7\text{-S})(\mu\text{-S}t\text{Bu})_9]$ (**27**) and $[\text{Ni}_{17}(\mu_5\text{-S})_3(\mu_3\text{-S})_2(\mu_3\text{-S}t\text{Bu})_6(\mu\text{-S}t\text{Bu})_9]$ (**29**) are investigated by UV/Vis spectroscopy, cyclovoltammetry as well as DFT-calculations for selected complexes.

- | | |
|--|---|
| • $[\text{Ni}_5(\mu_5\text{-S})(\mu\text{-S}t\text{Oct})_5][\text{BzEt}_3\text{N}]$ (23) | • $[\text{Ni}_2(\text{S}t\text{Oct})_2(\text{Ph}_3\text{P})_2]$ (19) |
| • $[\text{Ni}_5(\mu_5\text{-S})(\mu\text{-S}t\text{Pent})_5][\text{BzEt}_3\text{N}]$ (24) | • $[\text{Ni}_2(\text{S}t\text{Bu})_2(\text{Ph}_3\text{P})_2]$ (20) |
| • $[\text{Ni}_{14}(\text{S})_6(\mu_5\text{-S}t\text{Bu})_2(\mu\text{-S}t\text{Bu})_{10}][\text{Et}_4\text{N}]$ (28) | • $[\text{Ni}_2(\text{S}t\text{Bu})_2(\text{Ph}_3\text{P})_3]$ (21) |
| • $[\text{Ni}_{20}(\text{S})_{12}(\mu\text{-S}t\text{Bu})_{10}][(\text{NEt}_4)_2]$ (30) | |

Furthermore the reactions of *tert*-thiolate ligands with NHC-Ni(II)-precursors (NHC = N-heterocyclic carbenes) and Ni(II)-bromid afforded numerous mononuclear NHC-Nickel-

thiolate and dinuclear Nickel-thiolate complexes with unusual structural motifs, which have been structurally, spectroscopically and electrochemically characterized

- $[\text{Ni}(\text{SPent})_2(\text{NHC})_2]$ **(12)**
- $[\text{Ni}(\text{StOct})_2(\text{NHC})_2]$ **(13)**
- $[\text{Ni}(\text{SAd})_2(\text{NHC})_2]$ **(14)**
- $[\text{Ni}(\text{StBu})_2(\text{NHC})_2]$ **(15)**
- $[\text{Ni}(\text{NHC-CS}_2)_2(\text{I})_2]$ **(16)**
- $[\text{Ni}_2(\text{StOct})_6\text{K}_2(\text{DMF})_4]$ **(17)**
- $[\text{Ni}_2(\text{StOct})_6\text{K}_2(\text{CH}_3\text{CN})_2(\text{Ph}_3\text{PO})_2]$ **(18)**