

“Investigations on complex-chemical modeling of the active sites of the Nitrogenase”

Abstract:

The present thesis deals with mixed-valent iron-chalcogenide-chalcogenolate-complexes of the composition $[\text{Fe}_6\text{S}_9(\text{SR})_2]^{4\ominus}$ (R = Et, Bz), which shows great structural common characteristics with the active sites of the Nitrogenase, in particular the P-cluster and FeMo-Co-factor. Therefore, those $[\text{Fe}_6\text{S}_9(\text{SR})_2]^{4\ominus}$ -complexes have a very high potential for the synthesis of novel model compounds for the natural examples.

These $[\text{Fe}_6\text{S}_9(\text{SR})_2]^{4\ominus}$ -complexes are accessible through a synthesis way that was described in the literature as the disulphide route in 1982, using $\text{FeCl}_3/\text{NaSR}/\text{Na}_2\text{S}_2$ in a mole ratio of 1/3/1. In this thesis could be shown, that its yield depends very strongly of the employed alkali metal salts. The best yields of up to 84 % were achieved with lithium salts. Thus this synthesis method could be optimized too. During the use of sodium or potassium salts the yields decrease, lying between 35 % and 0 %. Within the scope of these investigations, five novel salts of the complex anion $[\text{Fe}_6\text{S}_9(\text{SR})_2]^{4\ominus}$ (R = Et, Bz) were isolated and characterized by x ray crystallography.

The up to now unknown selenolato-selenido-derivatives of the composition $[\text{Fe}_6\text{Se}_9(\text{SeR})_2]^{4\ominus}$ (R = Et, Bz) could be synthesized and characterized by x ray crystallography for the first time. In the dimer $[(\text{Fe}_6\text{Se}_9(\text{SeBz})_2)(\text{Na}_3(\text{MeOH})_4(\text{THF})_2)]^{5\ominus}$ two complex anions are combined through three sodium cations in a completely novel connection pattern. Additionally, the cyclic compound $[\text{Fe}_{13}\text{Se}_{20}(\text{OH})]^{5\ominus}$ could be isolated, which is of a novel member of a compound class designated in the literature as *ferric wheels*.

Conversions of the $[\text{Fe}_6\text{S}_9(\text{SBz})_2]^{4\ominus}$ -ion with the object to synthesize new model compounds were carried out intensely. For this purpose the $[\text{Fe}_6\text{S}_9(\text{SBz})_2]^{4\ominus}$ -ion was converted under different reaction conditions with various substrates containing iron in the oxidation states 0, +2 and +3. These conversions resulted in derivatives of the very stable cuban cluster $[\text{Fe}_4\text{S}_4(\text{X})_4]^{2\ominus}$ (X = SR, Cl, Br) and in the two-nuclear complex $[\text{Fe}_2\text{S}_2\text{I}_4]^{2\ominus}$.