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Mission: Darmstadt, Germany, from 01/08/2024 to 31/08/2024, group of Vera KREWALD

Objective: Training in DFT calculations with the specific target of gaining insights on the conversion of thiolate-supported iron-azido to iron-nitrido adducts.

Project: Thiolate-supported Fe-Nitrogen adducts relevant to the nitrogenase FeMo-co

The increasing demand for bioavailable nitrogen and sustainable ammonia production has driven researchers to investigate the mechanism of the Haber-Bosch process and nitrogenase enzymes<sup>1-3</sup>. Inspired by the FeMo-co, the active site of the nitrogenase enzymes, and the intermediates involved in the reduction of dinitrogen, my research focuses on the reactivity of thiolate-Fe complexes  $[\text{Fe}_2^{\text{S}}]$  and  $[\text{Fe}_2^{\text{SMe}}]^{2+}$  (Figure 1) with nitrogenase-relevant nitrogen ligands (such as  $\text{N}_2\text{H}_4$ ,  $\text{NH}_3$ ,  $\text{NH}_2^-$  and  $\text{N}^{3-}$ ). In the presence of sodium azide ( $\text{NaN}_3$ ), square-pyramidal  $\text{Fe}^{\text{II}}$ -thiolate azido complexes  $[\text{LFe}^{\text{II}}\text{N}_3]^-$  and  $[\text{LSMeFe}^{\text{II}}\text{N}_3]$  were obtained (Figure 1). In the literature, irradiation of M-azido complexes has been employed as synthetic pathway to M-nitrido formation, which is a key intermediate in the dinitrogen reduction cycle of FeMo-co<sup>4,5</sup>. Although initial promising results suggested that UV irradiation of the  $[\text{LFe}^{\text{II}}\text{N}_3]^-$  and  $[\text{LSMeFe}^{\text{II}}\text{N}_3]$  complexes might trigger some reactivity, experimental efforts were unsuccessful in obtaining the targeted Fe-nitrido complex.

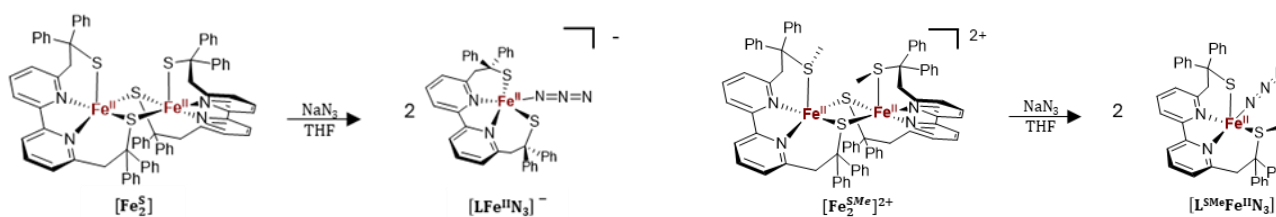


Figure 1. Fe-azido complexes synthesis from the corresponding initial  $[\text{Fe}_2^{\text{S}}]$  (left) and  $[\text{Fe}_2^{\text{SMe}}]^{2+}$  (right) complexes.

Hosted by Prof. Vera Krewald at the TU Darmstadt, a theoretical approach was adopted to investigate  $[\text{LFe}^{\text{II}}\text{N}_3]^-$  and  $[\text{LSMeFe}^{\text{II}}\text{N}_3]$ , as well as the targeted Fe-nitrido  $[\text{LFe}^{\text{IV}}\equiv\text{N}]^-$  and  $[\text{LSMeFe}^{\text{IV}}\equiv\text{N}]$  complexes. DFT and TD-DFT calculation were performed, and the following results were obtained:

- **Geometry optimization and frequency calculations:** optimised geometries closely reproduce distances and angles of the iron first coordination sphere of the SC-XRD structure considering packing effect in solid state. The IR spectra of the azido complexes were simulated and compared with experimental data. Similarly, the IR spectra of the nitrido complexes were simulated, predicting characteristic peaks expected experimentally.
- **Single point calculations and reaction thermodynamics:** the  $[\text{LFe}^{\text{II}}\text{N}_3]^-$  and  $[\text{LSMeFe}^{\text{II}}\text{N}_3]$  complexes were found to be more stable in high spin state ( $S=2$ ). The reaction energy profile for competitive processes (azide loss, photo-oxidation and photo-reduction) were evaluated: all light-induced reactions are endergonic, the photooxidation process is favourable in the case of  $[\text{LSMeFe}^{\text{II}}\text{N}_3]$  (azide loss being the competitive process at +10.3 kJ/mol) whereas azide loss is most favourable for  $[\text{LFe}^{\text{II}}\text{N}_3]^-$ .
- **TD-DFT (Figure 2 example  $[\text{LFe}^{\text{II}}\text{N}_3]^-$ ):** the UV-vis spectra were simulated and well reproduced the shape of the spectrum obtained experimentally. Transitions associated with the excitation bands were identified, especially the transition involving the excitation of the electron from the non-bonding orbitals to the perpendicular antibonding  $\pi$ -orbitals of the azide moiety ( $\text{nb} \rightarrow \pi^*$ ) which is responsible for the targeted cleavage of the  $\text{N}\alpha\text{-N}\beta$  azide bond. This was important for understanding the range of wavelengths that can potentially trigger productive photo-oxidation and nitrogen ejection (270-280 nm for  $[\text{LFe}^{\text{II}}\text{N}_3]^-$  and 275 - 300 nm for  $[\text{LSMeFe}^{\text{II}}\text{N}_3]$ ) and, consequently, for guiding subsequent experimental investigations.

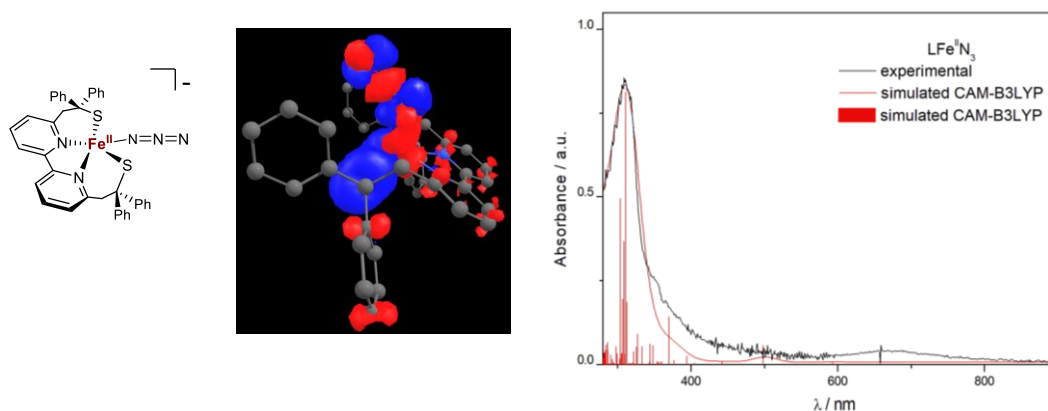


Figure 2. Difference in electron density map for the  $\text{nb} \rightarrow \pi^*$  transition of the azide moiety (270.8 – 280.7 nm range, middle) and experimental UV-vis spectra (left) of the  $[\text{LFe}^{\text{II}}\text{N}_3]^-$  complex (1 mM in THF, 1 cm o.l. in black) and UV-vis spectra predicted with TD-DFT at the CAM-B3LYP /def2-TZVP level of theory (red).

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