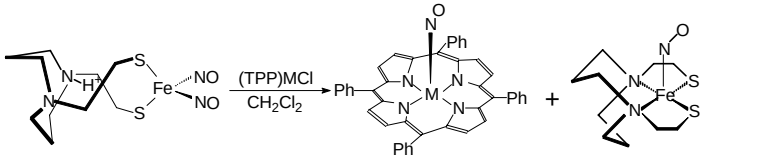
Iron Dinitrosyl Complexes: A Reaction Model for NO Transport and Transfer

Chao-Yi Chiang and Marcetta Y. Darensbourg

Department of Chemistry, Texas A&M University.

The important physiological roles of nitric oxide in living organisms are at odds with the indiscriminate reactivity of the free NO radical. Hence intricate control mechanisms are required for storage, transport and transfer of NO to its various biological targets. Among the proposed storage components are protein-bound thionitrosyls ($R_{protein}$-SNO) and protein-bound dinitrosyl iron complexes, DNIC's$_{protein}$. Current knowledge suggest the latter are derived from iron-sulfur cluster degradation in the presence of excess NO.[1] Mobilization of protein-bound NO could involve NO or $Fe(NO)_2$ unit transfer to small serum molecules such as glutathione or free cysteine.[2] As the stabilization of NO during transport and its release to targets is critical to the function of NO in biological systems, we have designed a reaction model study to address the fundamental properties of a prototypal iron dinitrosyl for NO storage, transfer and release.

While the bismercaptoethanediazocyclohexane, bme-daco, ligand typically binds in square planar N_2S_2 coordination, it acts as a bidentate dithiolate donor in an $Fe(NO)_2$ derivative.[3] The removal of NO produces the mono-NO complex, (bme-daco)Fe(NO) and simplifies studies of NO release mechanisms. We have explored the ability of (H^+bme-daco)$Fe(NO)_2$ to deliver nitric oxide to heme-type model complexes, Fe or Co porphyrins, and other NO uptake complexes such as $[(N_2S_2)Fe]_2$ (N_2S_2 = bme-daco and bme*-daco). The scope and preliminary mechanistic studies will be presented.



(H^+bme-daco)$Fe(NO)_2$ ν(NO): 1748, 1699 cm^{-1}

(bme-daco)Fe(NO) ν(NO): 1649 cm^{-1} in CH_2Cl_2

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