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A bridged di-iron porphyrin hyponitrite complex as a model for biological N_2O production from hyponitrite

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ABSTRACT

Heme-hyponitrites are intermediates that form at the bimetallic active sites of bacterial nitric oxide reductases. To probe a possible effect of the Fe–Fe distance on hyponitrite stability, we prepared a bridged bis-porphyrin Fe-hyponitrite compound, namely $[(OEP\text{-}CH_2)Fe]_2(\mu_2,\eta^1,\eta^1\text{-}ONNO)$. Its υ_{NO} of 992 cm^{-1} (υ_{15NO} of 976 cm^{-1}) is close to the υ_{NO} of 983 cm^{-1} reported previously by us for the crystallographically characterized $[(OEP)Fe]_2(\mu_2,\eta^1,\eta^1\text{-}ONNO)$ compound. The bridged bis-porphyrin Fe-hyponitrite complex is unstable with respect to N_2O production, supporting the role of the bis-Fe porphyrin system in hyponitrite conversion to N_2O. The preparation and crystallographic determination of the bridging sulfato derivative is also reported.

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1. Introduction

The mechanism by which bacteria utilize bimetallic heme/non-heme active sites to detoxify NO remains an active area of research. Crystallographic [1–3] and density functional theory calculations [4–6] have provided significant insight into the likely pathways by which the bimetallic active site of bacterial enzymes responsible for the coupling of two molecules of NO form hyponitrite intermediates en route to the non-toxic N_2O product that is a greenhouse gas [7]. Several mechanisms have been proposed for the bacterial NO coupling reaction [6,8,9], some of the most widely cited are shown as **A**, **B**, and **C** in Fig. 1.

The hyponitrite intermediates **D** (Fig. 1; M = Fe, Cu) have been characterized based on resonance Raman spectroscopy for a bacterial NO reductase [10] and caa_3 oxidoreductase [11]. The involvement of protons in hyponitrite formation, and hyponitrite decomposition to N_2O in the presence/absence of protons remain an intense area of study.

It is interesting to note that although hyponitrite complexes of coordination compounds are known [12,13], only two heme model-hyponitrite compounds have been reported to date [14,15], and only one has been structurally characterized. The first isolated hyponitrite-bridged iron heme model complex $[(OEP)Fe]_2(\mu_2,\eta^1,\eta^1\text{-}ONNO)$ was reported by us [14]. This compound releases N_2O gas upon reaction with the protic acid HCl, but also converts slowly at room temperature to the known (OEP)Fe(NO) nitrosyl. Importantly, (OEP)Fe(NO) does not self-couple to give the bimetallic hyponitrite species [14,15]. The molecular structure of $[(OEP)Fe]_2(\mu_2,\eta^1,\eta^1\text{-}ONNO)$ revealed that the bridged *trans*-hyponitrite ligand binds to two Fe centers though the hyponitrite O atoms (Fig. 2).

The non-bonding distance between the two Fe centers is ~6.7 Å, which is significantly longer than those in the bimetallic heme/non-heme active sites of NO reductases and cytochrome oxidases exhibiting NOR activity. For example, the distance between the heme-Fe and nonheme-Fe in the NO reductase from *Pseudommonas aeruginosa* is 3.8 Å [1]; the related distance between the heme-Fe and active-site Cu center in *Thermus thermophilus* cytochrome ba_3 is 4.4 Å [16]. The long Fe–Fe distance in $[(OEP)Fe]_2(\mu_2,\eta^1,\eta^1\text{-}ONNO)$ (Fig. 2) may well help favor the *O,O*-bonding mode of the hyponitrite bridge. The closely related iron porphyrin hyponitrite model compound $[(PPDME)Fe]_2(\mu_2,\eta^1,\eta^1\text{-}ONNO)$ was also reported by us [15].

To improve upon our approach to study heme-hyponitrite binding and reactivity, we sought to prepare di-Fe heme-

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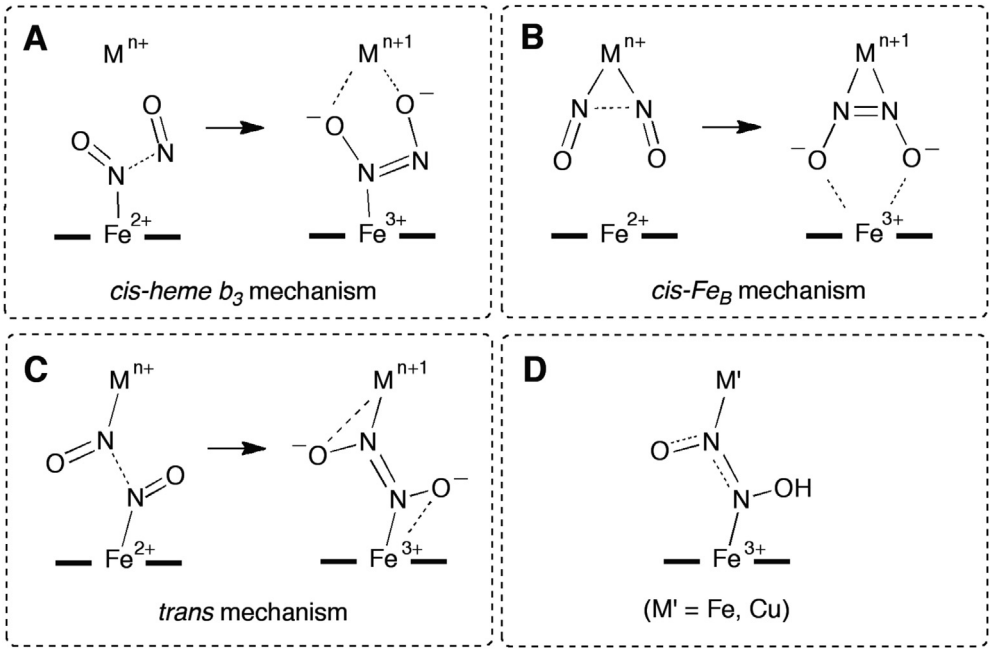

Fig. 1. Commonly proposed hyponitrite intermediates in bimetallic heme active sites.

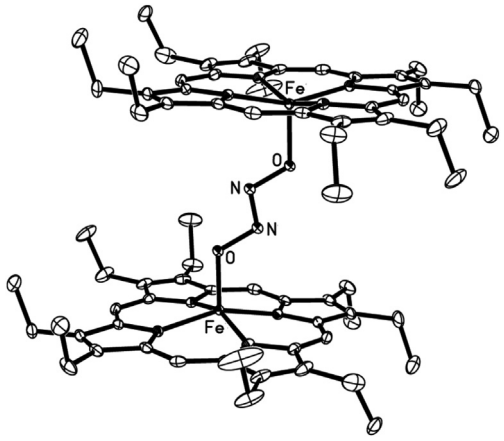

Fig. 2. The molecular structure of $[(OEP)Fe]_2(\mu_2,\eta^1,\eta^1$-ONNO) [14].

hyponitrite model compounds with potentially shorter Fe—Fe distances similar to those present in the bacterial NO reductases (~4 Å). In this paper, we report the preparation and thermal reaction of such a bridged porphyrin-hyponitrite complex.

2. Experimental section

All reactions were performed under an atmosphere of nitrogen using standard Schlenk glassware and/or in anaerobic and moisture-free glove box. Solutions for spectral studies were also prepared under a nitrogen atmosphere. Solvents were dried by passage through alumina (using a Pure Solv 400-5-MD system) and deaerated just prior to use. The $[(OEP\text{-}CH_2)Fe]_2(\mu\text{-}O)$ oxo-dimer (**1**) [17] and hyponitrous acid ($H_2N_2O_2$) [18] were prepared according to literature procedures. The ^{15}N-labeled $H_2^{15}N_2O_2$ was prepared using similar procedures as used for the unlabeled analog. Infrared spectra were recorded on a Bio-Rad FT-155 FTIR spectrometer.

2.1. Preparation of $[(OEP\text{-}CH_2)Fe]_2(\eta^1,\eta^1\text{-}O_2SO_2)$ (2)

To a CH_2Cl_2 solution (10 mL) of $[(OEP\text{-}CH_2)Fe]_2(\mu\text{-}O)$ (**1**; 8 mg, 0.006 mmol) was added an aqueous H_2SO_4 solution (0.25 mL, ~25x excess). The color of the stirred solution changed from green to brown overnight. The resulting dark brown powder (6 mg) was collected by filtration and dried in vacuo. The IR spectrum of the resulting solid indicated that it was a mixture of the product $[(OEP\text{-}CH_2)Fe]_2(\eta^1,\eta^1\text{-}O_2SO_2)$ (**2**) and the precursor $[(OEP\text{-}CH_2)Fe]_2(\mu\text{-}O)$ (**1**). The characteristic bands of sulfate anion [19,20] in the 980–1140 cm^{-1} range are obscured by the porphyrin bands. X-ray diffraction-quality crystals were grown at room temperature from a CH_2Cl_2/acetonitrile (1:2) solution.

2.2. Preparation of $[(OEP\text{-}CH_2)Fe]_2(\eta^1,\eta^1\text{-}ONNO)$ (3)

To a CH_2Cl_2 solution (10 mL) of $[(OEP\text{-}CH_2)Fe]_2(\mu\text{-}O)$ (**1**; 15 mg, 0.011 mmol) was added dropwise an excess of $H_2N_2O_2$ (~0.15 mmol in Et_2O). The color of the stirred solution changed from green to brown-green over a 30 min period. The solution was reduced to ~2 mL, and hexane(10 mL) was added to precipitate the product. IR (NaCl disk): $\upsilon NO = 992\ cm^{-1}$. The ^{15}N-labeled $[(OEP\text{-}CH_2)Fe]_2(\eta^1,\eta^1\text{-}O^{15}N^{15}NO)$ analog was prepared similarly using the $H_2^{15}N_2O_2$ reagent. IR (NaCl disk): $\upsilon^{15}NO = 976\ cm^{-1}$.

X-ray diffraction data for compound **2** were collected at 100(2) K using Mo Kα (λ = 0.71073 Å) radiation. Tables of bond lengths and angles are contained in the Supporting Information. CCDC 1428275 (compound **2**) contains the supplementary crystallographic data. These data can be obtained free of charge from the Cambridge Crystallographic Data Center via http://www.ccdc.cam.ac.uk/conts/retrieving.html.

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