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Iron-porphyrin coordinates an arginine guanidine side-chain in a protein pocket –Insights from microspectrophotometry and crystallography

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Nitrophorin 4 (NP4) is a ferriheme protein that is found in the saliva of the blood-sucking insect Rhodnius prolixus. The purpose of the protein is to transport NO from the saliva of the insect into the tissue of a victim, for which purpose the heme iron is maintained in the Fe(III) state. A novel protein mutant NP4(L130R) was generated to explore the recently reported nitrite disproportionation reaction of nitrophorins. It is expected to have the positively charged guanidine group close to or in the distal site of the heme pocket. The protein was crystallized and the X-ray structure was solved. Unexpectedly, the Arg130:N atom appeared to coordinate the heme iron. However, studies of the protein by UV/Vis absorption and resonance Raman (RR) spectroscopy in solution did not suggest Arg coordination. Microspectrophotometry performed at crystals under synchrotron radiation revealed that under the rapid photon induced reduction via X-ray, Arg130 coordination is enabled upon reduction to Fe(II). This can be rationalized by the stronger Lewis acidity of Fe(III) compared to Fe(II). Overall, this appears to be the first description of a metalloporphyrin-guanidine coordination complex and the third example of a metal-guanidine coordination in a biomolecule. This is the more remarkable because deprotonation of the guanidinium group is difficult to accomplish in aqueous media, but becomes apparently possible in the protein pocket of NP4.

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