

Formation of Nitrosyl-Iron(II) β -Oxoporphyrin π -Cation Radical Complexes. Models for a Reaction Intermediate of Dissimilatory Nitrite Reductases

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One-electron oxidation of nitrosyl-iron(II) β -oxoporphyrin complexes, models for haem d_1 , with silver hexafluoroantimonate yields the corresponding π -cation radicals, characterized by electronic absorption and IR spectroscopies.

Cytochrome cd_1 are dissimilatory nitrite reductases found in many denitrifying bacteria¹⁻³ catalysing the reduction of nitrite.⁴ The enzyme contains haems c and d_1 as the prosthetic group, while haem d_1 was identified as the preferential site for ligand binding and for catalysis.⁵ The structure of haem d_1 has been proposed to be iron dioxoisobacteriochlorin.⁶

During the reduction of NO_2^- to NO or N_2O , a nitrosyl complex $[\text{Fe}^{\text{II}}\text{NO}]^+$ formed by dehydration of NO_2^- has been postulated^{7,8} to be a reaction intermediate, Scheme 1.

Possible descriptions of the $[\text{Fe}^{\text{II}}\text{NO}]^+$ state are $\text{Fe}^{\text{II}}\text{NO}$ π -cation radical, $\text{Fe}^{\text{II}}(\text{NO})^+$, and $\text{Fe}^{\text{III}}\text{NO}$. Alternatively, the $[\text{Fe}^{\text{II}}\text{NO}]^+$ intermediate can be prepared by one-electron oxidation of a nitrosyl-iron(II) complex. Model studies have shown that an $\text{Fe}^{\text{II}}\text{NO}$ π -cation radical complex is formed upon oxidation of the nitrosyl-iron(II) complex of isobacteriochlorin (iBC), a model for sirohaem,[†] in contrast to the $\text{Fe}^{\text{III}}\text{NO}$ formation by employing porphyrin derivatives.^{8b,c} Although introduction of oxo groups to the macrocycle periphery was reported to significantly change the redox properties of iBC and make the oxo derivatives more akin to porphyrins,¹¹ effects of the oxo groups on the structure of the intermediate have not been examined yet. It is therefore important to determine and characterize the $[\text{Fe}^{\text{II}}\text{NO}]^+$ intermediate of dioxo iBC by using synthetic model complexes.

We report here one-electron oxidation of nitrosyl-iron(II) complexes of oxochlorin \ddagger **1** and dioxoisobacteriochlorin **2**

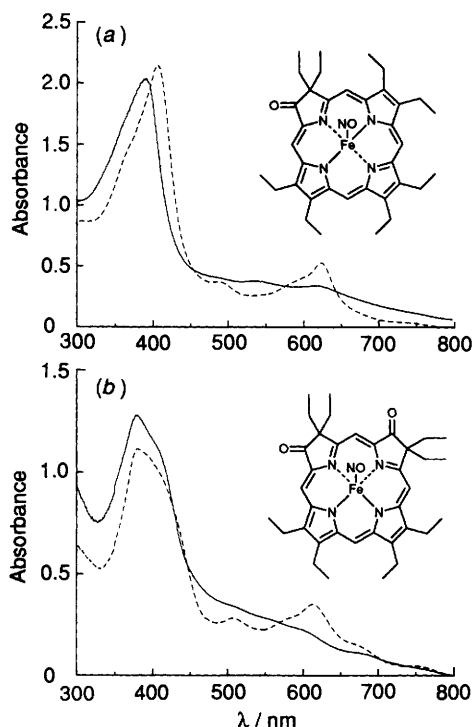


Fig. 1 Electronic absorption spectral changes upon addition of silver hexafluoroantimonate (1 equiv.) to dichloromethane solutions of oxochlorin, **1** [(a) dashed line] and dioxo iBC, **2** [(b) dashed line]. The resultant spectra of **3**(a) and **4**(b) are shown as solid line.

with silver hexafluoroantimonate, and characterization of the oxidation products **3** and **4** by electronic absorption and IR spectroscopies. It has been shown that both **3** and **4** are $\text{Fe}^{\text{II}}\text{NO}$ π -cation radical complexes with the bent $\text{Fe}-\text{NO}$ bonds.

Chemical oxidation of **1** and **2**§ has been performed with silver hexafluoroantimonate (AgSbF_6) (1 equiv.) in dichloromethane under an argon atmosphere.¶ The oxidation of **1** causes a small shift of the Soret band, loss of the characteristic band for chlorin complexes at ca. 600 nm, and appearance of weak broad bands stretching into the near-IR region to yield an entirely new species, **3** [Fig. 1(a)]. The oxidation of **2** gives a new complex, **4**, with similar spectral changes [Fig. 1(b)]. The absorption spectra of **1** and **2** are completely recovered by the reduction with tetra-*n*-butylammonium iodide (TBAI), indicating that the NO ligands remain in the redox process. The spectral features of **3** and **4** are characteristic of chlorin and isobacteriochlorin π -cation radical complexes.^{8b,c,12-14} Further, **3** and **4** are ESR silent even at 77 K,|| as observed for

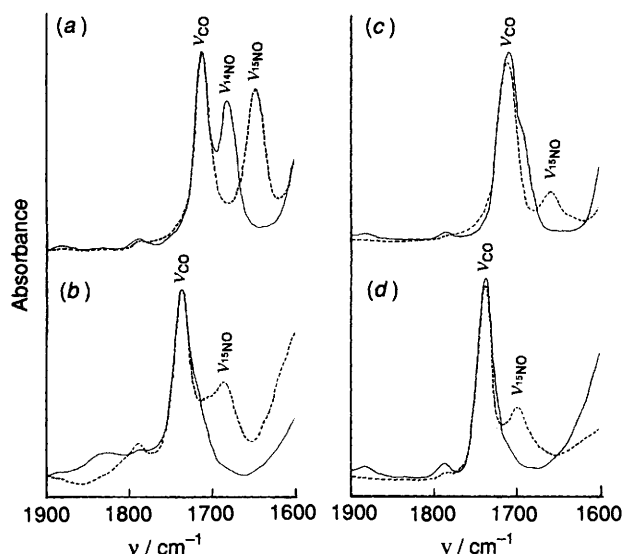
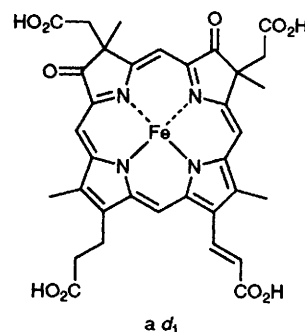
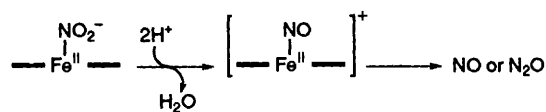
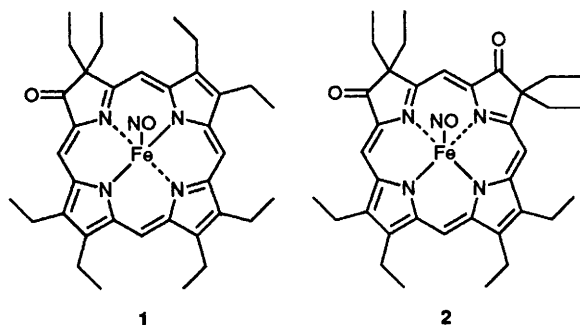


Fig. 2 IR spectra of nitrosyl-iron complexes (**1-4**) in dichloromethane with NaCl windows (2 cm^{-1} resolution). (a) oxochlorin, **1**; (b) the oxidation product, **3**; (c) dioxo iBC, **2**; (d) the oxidation product, **4**. The corresponding spectra of ^{15}NO derivatives are shown as dashed line.





Scheme 1



OEC and OEiBC π -cation radicals of $\text{Fe}^{\text{II}}\text{NO}$ complexes.^{8b,c} Thus, **3** and **4** are reasonably formulated to be the $\text{Fe}^{\text{II}}\text{NO}$ π -cation radical complexes.

To confirm the electronic structures of **3** and **4**, IR spectral measurements have been made. Upon oxidation of **1**, the CO band shifts from 1712 **1** to 1737 cm^{-1} **3** [Fig. 2(a) and (b)]. While the ^{14}NO band of **3** would be a shoulder on the CO band (ca. 1720 cm^{-1}), the existence of the NO ligand in **3** was established by the observation of ^{15}NO band at 1686 cm^{-1} [Fig. 2(b), dashed line]. This band of **3** falls within the range of N–O vibrations for $\text{Fe}^{\text{II}}\text{NO}$ and $\text{Fe}^{\text{II}}\text{NO}$ π -cation radical complexes with bent Fe–NO bonds, rather than for $\text{Fe}^{\text{III}}\text{NO}$ and $\text{Fe}^{\text{II}}(\text{NO})^+$ complexes having linear Fe–NO bonds.^{8b,c,15,16} Further, a large oxidation-induced shift of the CO band ($\Delta\nu$ 25 cm^{-1}) indicates that the oxidation of **1** to **3** accompanies a significant change of the electronic structure of the macrocycle, consistent with the π -cation radical formation.** **2** and **4** exhibit similar IR spectral features as demonstrated in Fig. 2(c, d), in which the large shift of the CO band ($\Delta\nu$ 25 cm^{-1}) by the oxidation and the ^{15}NO bands at 1663 **2** and 1700 **4** cm^{-1} are observed. Therefore, we conclude that the one-electron oxidation products of **1** and **2** are the $\text{Fe}^{\text{II}}\text{NO}$ π -cation radicals **3** and **4** with the bent Fe–NO bonds, instead of the $\text{Fe}^{\text{III}}\text{NO}$ observed for the OEP complex.^{8b,15,17}

The production of $\text{Fe}^{\text{III}}\text{NO}$ and $\text{Fe}^{\text{II}}\text{NO}$ π -cation radical would be determined by the relative energy levels of the iron d ($\text{Fe}(d_{z^2})\text{-NO}(\sigma_{\text{N}})$ hybrid orbital) and the macrocycle π -orbitals.^{8c} Since the ring oxidation potentials for the free-bases of oxochlorin (0.84 V) and dioxo iBC (0.82 V) are almost identical to that of porphyrin (0.83 V),^{11a} the Fe–NO hybrid orbitals of **1** and **2** should become much lower energy levels by the introduction of the oxo groups, to make **3** and **4** π -cation radicals. The stabilization of the iron d orbitals of the oxo derivatives is consistent with MO calculation and redox results.^{11a,b} The model studies presented here provide the first structural model for the putative reaction intermediate of dissimilatory nitrite reductases.

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Footnotes

† Sirohaem is the prosthetic group in assimilatory nitrite reductases of spinach⁹ and *Neurospora crassa*.¹⁰

‡ Abbreviations: OEP, 2,3,7,8,12,13,17,18-octaethylporphyrin; OEC, 7,8-dihydro-2,3,7,8,12,13,17,18-octaethylporphyrin (octaethylchlorin); OEiBC, 2,3,7,8-tetrahydro-2,3,7,8,12,13,17,18-octaethylporphyrin (octaethylisobacteriochlorin); oxochlorin, 3-oxo-2,2',7,8,12,13,17,18-octaethylporphyrin, dioxoisobacteriochlorin (dioxo iBC), 3,8-dioxo-2,2',7,7',12,13,17,18-octaethylporphyrin.

§ Free-bases of oxochlorin and dioxo iBC were prepared by a published method: C. K. Chang, C. Sotiriou and W. Wu, *J. Chem. Soc., Chem. Commun.*, 1986, 1213. Nitrosyl-iron(II) complexes (**1** and **2**) and their ^{15}NO derivatives were obtained as previously described.^{8c}

¶ **1** and **2** exhibit reversible one-electron oxidation at 0.76 and 0.74 V (vs. SCE), respectively, which are ca. 100 mV positive-shifted from $\text{OEPFe}^{\text{II}}\text{NO}$ (0.65 V).

|| Upon reduction of **3** and **4**, typical three-line ESR spectra of the $\text{Fe}^{\text{II}}\text{NO}$ complexes (**1** and **2**) were reproduced.

** The π -cation complexes of zinc(II) oxochlorin and dioxo iBC also exhibit the large oxidation-induced shifts of the CO bands from 1707 to 1734 cm^{-1} ($\Delta\nu$ 27 cm^{-1}) and from 1711 to 1734 and 1755 cm^{-1} ($\Delta\nu$ 23 and 44 cm^{-1}), respectively.

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