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## Q26

# Preparation and Structural Characterization of Nitrosyl Complexes of Ferric Porphyrinates

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Nitrosyl complexes of ferric porphyrinates have been prepared by reaction of perchloratoporphinatoiron(III) complexes with nitric oxide. Two species have been structurally characterized: aquonitrosyl(*meso*-tetraphenylporphinato)iron(III) perchlorate, [Fe(TPP)(NO)($H_2O$)]$ClO_4$, and nitrosyl(octaethylporphinato)iron(III) perchlorate, [Fe(OEP)(NO)]$ClO_4$.

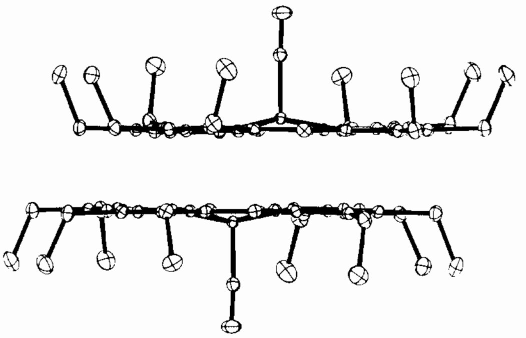

Fig. 2. The $\pi-\pi$ dimer in the solid state.

Crystal data: [Fe(TPP)(NO)($H_2O$)]$ClO_4$, monoclinic, $a$ = 10.303(2) Å, $b$ = 8.124(2) Å, $c$ = 21.364(8) Å, and $\beta$ = 97.76(2)°, $Z$ = 2, space group $P2_1/n$, 3999 observed data, $R_1$ = 0.057, $R_2$ = 0.079, all measurements at 96 K. [Fe(OEP)(NO)]$ClO_4$, monoclinic, $a$ = 12.890(2) Å, $b$ = 20.363(3) Å, $c$ = 14.969(2) Å, and $\beta$ = 95.48(2)°, $Z$ = 4, space group $P2_1/n$, 5956 observed data, $R_1$ = 0.058, $R_2$ = 0.063, all measurements at 292 K.

All complexes are low-spin $\{FeNO\}^6$ species. [Fe(OEP)(NO)]$ClO_4$ is the first five-coordinate low-spin ferric porphyrinate to be structurally characterized. The Fe–N–O moiety is essentially linear in both species. For [Fe(TPP)(NO)($H_2O$)]$ClO_4$, Fe–$N_p$ =

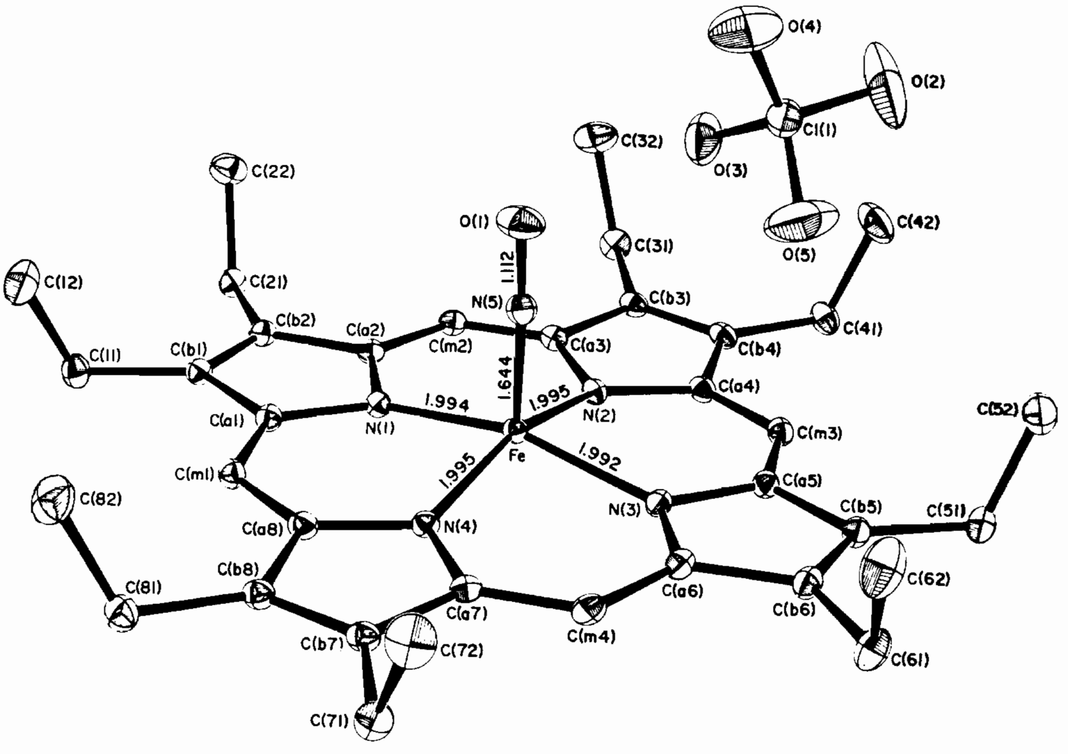

Fig. 1. Structure of [Fe(OEP)(NO)]$ClO_4$.

1.999(6) Å, Fe–N(NO) = 1.652(5) Å, and Fe–O = 2.001(5) Å. For [Fe(OEP)(NO)]$ClO_4$ (Fig. 1), Fe–$N_p$ = 1.994(1) Å, Fe–N(NO) = 1.644(3) Å; the iron(III) atom is displaced 0.29 Å from the mean plane of the porphinato core. The structural parameters of both complexes are appropriate for low-spin ferric porphyrinates. [Fe(OEP)(NO)]$ClO_4$ forms a remarkable $\pi$–$\pi$ dimer in the solid state (Fig. 2). The two planar cores are parallel with an interplanar separation of only 3.36 Å.

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## Q27

## Corrinoid Catalysis of Thiol Oxidation

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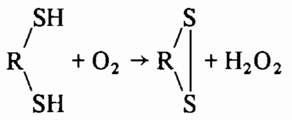
Under appropriate conditions, thiols can react with corrinoids to form relatively stable complexes [1–7], or reduced corrinoids [1, 2, 8–11]. If alkyl halides are present during the reduction of corrinoids by thiols, alkyl corrinoids are produced [4, 9, 12, 13]. In the presence of oxidizing substrates, corrinoids will efficiently catalyze the oxidation of thiols to their corresponding disulfides [14–18]. In view of the important role that enzyme sulfhydryl groups play in corrinoid–coenzyme-dependent catalysis [19, 20], we have further characterized aerobic thiol oxidation catalyzed by a selected group of biologically important corrinoids and have determined the stoichiometry of the reaction.

Hydrogen peroxide and superoxide have been identified as reaction products during the aerobic catalysis of 2-mercaptoethanol [ME, 21] by the corrinoids listed in Table I. The reactions were conducted in a polarographic cell equipped with a Clark $O_2$ electrode [22]. The corrinoids used to initiate the reactions were prepared as described previously [23, 24] and their purity was determined by hplc [25]. $H_2O_2$ was detected by adding catalase to the reaction system. This resulted in an abrupt increase in $O_2$ concentration which is consistent with the catalytic activity of the enzyme. As anticipated, the pseudo-first order rate constant ($k_1$) of $O_2$ consumption in the presence of catalase decreased 50 per cent. Using a similar approach, superoxide dismutase was used in an attempt to detect the presence of $O_2^-$ as a reaction product. This was unsuccessful except for one corrinoid, namely Aq-Cbl (Table I). Thus, during the catalysis of ME oxidation by Aq-Cbl, $O_2^-$ is the primary reaction product. In the presence of dismutase, $k_1$ for the Aq-Cbl-catalyzed reaction decreased approximately 50 per cent which is consistent with the catalytic activity of this enzyme. $H_2O_2$ was also detected during Aq-Cbl-catalyzed oxidation of ME and may have been produced by the spontaneous dismutation of $O_2^-$.

Disulfide bond formation was monitored spectrophotometrically [26] during the oxidation of DTE. Pseudo-first-order rate constants for $O_2$ disappearance and for $DTE_{ox}$ appearance were in good agreement (Table II). These results, which differ from previously published studies [16, 17, 27], suggest that the reactions and their stoichiometries for aerobic oxidation of mono- and dithiols by corrinoids are:

$$2\,RSH + O_2 \rightarrow RSSR + H_2O_2 \qquad (1)$$



$$R\begin{matrix}\diagup SH\\ \diagdown SH\end{matrix} + O_2 \rightarrow R\begin{matrix}\diagup S\\ \diagdown S\end{matrix} + H_2O_2$$

(2)

TABLE I. Pseudo-First-Order Rate Constants, pH Optima, Products and Photosensitivity for Catalysis of ME Oxidation by Corrinoids.[a]

| Group | Catalyst | $k_1$, $sec^{-1}$ | pH Optimum | Reduced Product | $k_1$, $sec^{-1}$ (after photolysis)[b] |
|---|---|---|---|---|---|
| I | Ado-Cbl | 0.003 | Broad | $H_2O_2$ | 0.102 (20 sec) |
| | Me-Cbl | 0.003 | 7.0[c] | $H_2O_2$ | 0.184 (20 sec) |
| II | CN-Cbl | 0.080 | 8.0[c] | $H_2O_2$ | 0.080 (60 sec) |
| | Aq-Cbl | 0.180 | 8.4 | $HO_2$ | 0.180 (20 sec) |
| | Ado-Cbi | 0.23 | | $H_2O_2$ | 177.0 (60 sec) |
| | Me-Cbi | 0.56 | 11–13 | $H_2O_2$ | 122.0 (90 sec) |
| III | CN-Cbi | 191 | 8.5–9.5 | $H_2O_2$ | 190.0 (30 sec) |
| | $(Aq)_2$-Cbi | 211 | 8.8 | $H_2O_2$ | 210.0 (60 sec) |

[a] ME = 2.5 × $10^{-2}$ *M*; 25 ± 0.2 °C. [b] At the midway point of $O_2$ consumption, the polarographic cell was irradiated with light from a tungsten-filament high intensity lamp for the time indicated. [c] Measurement was made at the indicated pH only.