port U9B of the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory (BNL). The other[8] is of generally similar design except for its use of a conventional deuterium discharge Hinteregger light source. The instruments gave similar spectra except that the signal-to-noise ratio is significantly better with the synchrotron light source.

Figure 2 is a direct tracing of the spectrum obtained at BNL. There is a negative band at 208 nm with a molar ellipticity $[\theta] = -1.58 \times 10^3$ deg cm^2 dmol^{-1}, a positive band at 190 nm with $[\theta] = +3.37 \times 10^3$ deg cm^2 dmol^{-1}, and a negative band at 175 nm with $[\theta] = -3.47 \times 10^3$ deg cm^2 dmol^{-1}. The CD of heparins above 185 nm has been measured previously[9-13] (Table I). Sample heterogeneity (see above) is the most likely source of the relatively wide range of values observed.

The molar ellipticity of heparin at 210 nm is substantially less than the sum of monomeric constituents, the molar ellipticity of the iduronic acid moiety alone being -5.43×10^3 deg cm^2 dmol^{-1}.[17] The source of this nonadditivity at 210 nm may lie in a difference in position of equilibrium between the two ring conformations of the iduronic acid moiety. In the $^1C_4$ (L) ring conformation the carboxyl group is located equatorially and the four oxygen atoms axially; in the $^4C_1$ conformation the situation is reversed. Proton and carbon-13 NMR evidence[18] indicates that the $^1C_4$ conformation, or a slightly distorted form of it, occurs in solutions of heparin, and the $^1C_4$ form is also favored in methyl-L-idopyranuronosides. However, as Morris et al.[17] have pointed out, even a small proportion of methyl idopyranuronosides in the $^4C_1$ form might contribute an inordinately large CD to the monomer spectrum if that form is intensely optically active by virtue of the axial position of the carboxyl chromophore.

The positive dichroism near 190 nm originates in the π–π^* transitions of the uronic acid carboxyl chromophore and the hexosamine acetamido and sulfamino chromophores.[13] A correlation between positive 190-nm CD and (1→4)-linked amino sugars has been noted before.[13,15,19]

The negative CD at 175 nm is the first case of a discrete CD band being observed in aqueous solutions of a glycosaminoglycan below 180 nm. Stipanovic and Stevens[4] measured the VUCD of chondroitin and chondroitin-6-sulfate in aqueous solution and observed increasing negative ellipticity below 190 nm to the limits of those measurements near 170 nm. Hyaluronic acid measurements have been reported to 180 nm.[15,20]

Spectra of glycopyranoses,[21] glycopyranosides,[22] and cyclic ethers[23] provide evidence for an optically active transition near 175 nm associated with the unsubstituted sugar ring. The partial correlation of the sign of the 175-nm CD with anomeric configuration in glycopyranosides[22] implicates the linkage oxygen as one important determinant of CD, but its role could be either as the chromophore itself or as a dominant perturber of the actual chromophore (e.g., the ring oxygen).

In glycosaminoglycans, high-energy transitions of the substituent acetamido and carboxyl groups are also potential sources of optical activity of 175 nm. Assignment of the 175-nm dichroism in glycosaminoglycans will therefore be difficult because of the large number of electronic transitions which are potential sources of dichroism. Correlation of CD sign and magnitude with structural features, based on an accumulation of VUCD data, can be expected to help the development of proper assignments.

Comparing the 175-nm dichroism of heparin with that of chondroitins (Table I) indicates that the major source of the 175-nm dichroism may not be a substituent group, since the sign of CD does not correlate with hexosaminidic linkage, as does the π–π^* transition at 190 nm (see above). If the sign and magnitude of the 175-nm band proves to have its parentage largely in the ring and linkage oxygen chromophores, that band would then be an important spectroscopic indicator of glycosaminoglycan conformation in solution.

Acknowledgment. This work was supported by NIH Grant GM24862 and NATO Grant 705/83. The NSLS is supported by the Divisions of Material Sciences and Chemical Sciences and the U9B vacuum CD spectrometer by the Division of Health Effects Research, U. S. Department of Energy.

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Oxidation of Red Ferryl $[(Fe^{IV}O)^{2+}]$ Porphyrin Complexes to Green Ferryl $[(Fe^{IV}O)^{2+}]$ Porphyrin Radical Complexes

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Ferryl $(Fe^{IV}O)^{2+}$ porphyrin complexes are widely accepted as important constituents of the reactive forms of a variety of heme proteins including the peroxidases[1] and cytochromes P-450.[2] Model compounds for these two different oxidation states have been prepared as transient intermediates. Six-coordinate complexes, $BP(Fe^{IV}O)$ (B = *N*-methylimidazole, P = porphyrin dianion), have been prepared by reacting PFe^{II} with dioxygen (at −80 °C) to produce $PFe^{III}OOFe^{III}P$ followed by treatment with B.[3] These have physical properties that match those of the reactive intermediate, II, of horseradish peroxidose.[3-6] A related red, five-coordinate complex, $TMP(Fe^{IV}O)$, (TMP = dianion of tetramesitylporphyrin) is formed when the corresponding peroxo complex $TMPFe^{III}OOFe^{III}TMP$ is warmed to −30 °C.[7] The reaction between *m*-chloroperoxybenzoic acid and $TMPFe^{III}Cl$ at −78 °C produces the more highly oxidized green intermediate $(TMP\cdot)(Fe^{IV}O)X$ (X = monoanion) which has been formulated as containing a porphyrin π radical.[8] This green compound has been proposed as a model for horseradish peroxidase, I. While

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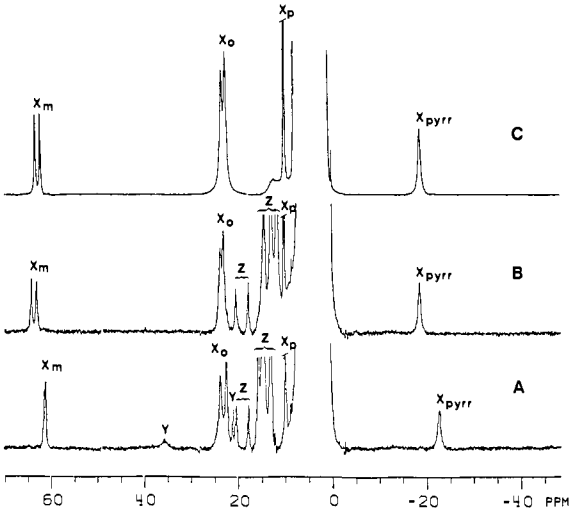
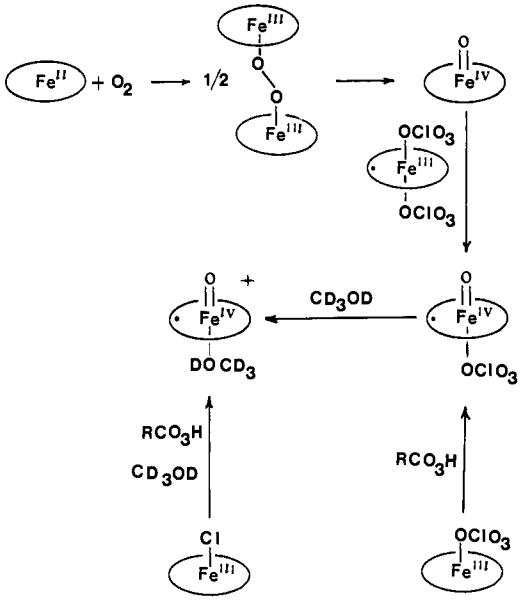


Figure 1. Proton NMR Spectra (360 MHz) of touluene-d_8 solutions of iron porphyrins at −70 °C. Trace A: a sample of TMP($Fe^{IV}O$), prepared via the sequence $TMPFe^{III}Cl + Zn/Hg \rightarrow TMPFe^{II}$, $2TMPFe^{II} + O_2 \rightarrow TMPFe^{III}OOFe^{III} \rightarrow 2TMP(Fe^{IV}O)$ after treatment with a small excess of $(TMP\cdot)Fe(ClO_4)_2$. Trace B: the same sample as in trace A after the addition of methanol to give ~4/1 toluene-d_8/methanol-d_4 v/v. Trace C: a sample of $TMPFe^{III}Cl$ in 4/1 toluene-d_8/methanol-d_4 v/v after treatment with *m*-chloroperoxybenzoic acid. Resonances X are assigned to $(TMP\cdot)(Fe^{IV}O)ClO_4$, Y to $(TMP\cdot)Fe^{III}(ClO_4)_2$, and Z to $TMPFe^{III}X$. Subscripts indicate resonance assignments: pyrr, pyrrole protons; o, *o*-methyl protons; m, *m*-phenyl protons; p, *p*-methyl protons. Additional resonances due to $(TMP\cdot)Fe^{III}(ClO_4)_2$ and $TMPFe^{III}X$ are observed in regions outside the window shown as required. The tops of the peaks labeled X_p have been cut off to allow reasonable display of the spectra.

these intermediates occur in two levels of oxidation and they should be interconverted by redox reactions, no previous demonstration of this has been reported.

Oxidation of toluene solutions containing $TMP(Fe^{IV}O)$ at −70 °C by chlorine, bromine, or $(TMP\cdot)Fe^{III}(ClO_4)_2$[9,10] is accompanied by the loss of the NMR resonances of $TMP(Fe^{IV}O)$[11] and the growth of resonances due to $(TMP\cdot)(Fe^{IV}O)X$.[11] Figure 1 gives the results of one experiment. Trace A shows a sample prepared from $TMP(Fe^{IV}O)$ and a slight excess of $(TMP\cdot)Fe(ClO_4)_2$. Peaks labeled X are due to the newly formed oxidation product, $(TMP\cdot)(Fe^{IV}O)ClO_4$. On warming, these peaks all decay together. The peaks, labeled Y are due to $(TMP\cdot)Fe(ClO_4)_2$. The peaks labeled Z are due to the meta H of various iron(III) complexes (TMPFeX, X = Cl, OH, ClO_4) which are present as a consequence of the intrinsic instability of $TMP(Fe^{IV}O)$.[7] Trace B shows the effect of adding methanol to sample A. Significant shifts in the resonance positions occur (presumably because of a change in one axial ligand from perchlorate to methanol) but the shift pattern is retained. Trace C shows a separate sample prepared by the addition of *m*-chloroperoxybenzoic acid to $TMPFe^{III}Cl$ in toluene/methanol (4/1, v/v) at −70 °C.[12,13] The similarity of the peaks labeled X in traces B and C indicated that a common species is present. Resonance assignments in Figure 1 have been based on relative intensities and comparison with spectra obtained from pyrrole-deuterated TMP. The splitting of the meta H and *o*-methyl resonances is indicative of two different axial ligands in $(TMP\cdot)(Fe^{IV}O)X$.[14-17] In a related experiment, treatment of $TMPFe^{III}ClO_4$ with *m*-chloroperoxybenzoic acid at −70 °C produces the same X spectrum as shown in trace A of Figure 1. These transformations are summarized in Scheme I.

Scheme I



Electron exchange between $TMP(Fe^{IV}O)$ and $(TMP\cdot)(Fe^{IV}O)X$ is slow on the NMR time scale. When a substoichiometric amount of bromine is added to $TMP(Fe^{IV}O)$ separate resonances are observed for $TMP(Fe^{IV}O)$ and $(TMP\cdot)(Fe^{IV}O)X$. Consequently the rate constant for exchange is much less than 4×10^4 s^{-1}.

In separate experiments we have verified that the formation of $(TMP\cdot)(Fe^{IV}O)X$ by these oxidation reactions occurs only when $TMP(Fe^{IV}O)$ is present. Reactions of $TMPFe^{III}Cl$, $TMPFe^{III}OH$, or $TMPFe^{III}OOFe^{III}TMP$ with these oxidizing agents do not produce the NMR resonances characteristic of $(TMP\cdot)(Fe^{IV}O)X$. Attempts to oxidize $BP(Fe^{IV}O)$ have lead only to its destruction probably because of oxidation of the amine. We have observed that $(TMP\cdot)(Fe^{IV}O)X$ is reduced by *N*-methylimidazole. Iodine is not a sufficiently strong oxidant to effect the oxidation of $TMP(Fe^{IV}O)$. Chlorine, bromine, or iodine alone are not capable of oxidizing $TMPFe^{III}ClO_4$ to the π radical $(TMP\cdot)Fe^{III}ClO_4X$. As a consequence of these observations it is possible to rank the order of redox potentials for these couples as follows: $I_2/I^- < (TMP\cdot)(Fe^{IV}O)X/TMP(Fe^{IV}O) < Br_2/Br^- < Cl_2/Cl^- < (TMP\cdot)Fe(ClO_4)_2/TMPFeClO_4$ with $(TMP\cdot)Fe(ClO_4)_2$ being the strongest oxidizing agent.

Since some peroxidazes are capable of oxidizing bromide or chloride,[18] environmental effects, including porphyrin structure

(9) $(TMP\cdot)Fe(ClO_4)_2$ was prepared by a modification of the method of Marchon and co-workers from $TMPFe^{III}OH$ and $Fe(ClO_4)_3\cdot 6H_2O$ and characterized by it electronic and ^1H NMR spectra (pyrrole, 40.6; meta, 58.4; *o*-methyl, 21.1; *p*-methyl, 12.9 ppm in toluene-d_8 at 24 °C).

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(12) The order of addition of reagents in these experiments is critical for their success. $TMP(Fe^{IV}O)$ is unstable in the presence of methanol and consequently its oxidation must be accomplished without methanol present. In toluene we find that addition *m*-chloroperoxybenzoic acid to $TMPFe^{III}Cl$ causes rapid bleaching of the porphyrin unless methanol is present. Since this latter effect is not seen if $TMPFe^{III}Br$ or $TMPFe^{III}OH$ is used instead of $TMPFe^{III}Cl$, we presume that methanol assists in removal of the coordinated chloride.[13]

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and axial ligation, must be able to modulate reactivity toward halide ions of the (P·)(Fe^{IV}O)X/P(Fe^{IV}O) couple in proteins. It is interesting to note, however, that the remarkable reactivity of (TMP·)(Fe^{IV}O)X toward hydrocarbons[8] is not reflected in an especially high one-electron redox potential.

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Registry No. TMP(Fe^{IV}O), 93085-16-6; (TMP·)Fe^{III}(ClO$_4$)$_2$, 93842-71-8; (TMP·)(Fe^{IV}O)Cl, 95724-71-3; (TMP·)(Fe^{IV}O)Br, 95724-72-4; (TMP·)(Fe^{IV}O)ClO$_4$, 95724-73-5; TMPFeCl, 77439-21-5; TMPFeOH, 77439-20-4; TMPFeClO$_4$, 93862-22-7; Cl$_2$, 7782-50-5; Br$_2$, 7726-95-6; *m*-chloroperoxybenzoic acid, 937-14-4.

Carbon Dioxide and Formaldehyde Coordination on Molybdenocene to Metal and Hydrogen Bonds of the C_1 Molecule in the Solid State

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Fixation of carbon dioxide and formaldehyde in their intact form on a metal center is a primary goal in metal-promoted transformations of a C_1 molecule, provided it forms metal–carbon bonds. Formation of formaldehyde[1,2] and carbon dioxide complexes[3] is, however, a quite rare reaction, in spite of the various strategies applied so far. Some to be mentioned utilized metal-carbenes, metal-nucleophiles, and bifunctional complexes.[1-3] All these compounds must possess a special ensemble of properties which seems very difficult to match and which are different for carbon dioxide and formaldehyde.

Coordination of formaldehyde has been achieved by a few complexes only,[1,2] all having a carbene-type reactivity by which they add to a >C=O double bond. Dicyclopentadienylmolybdenum(II)[4] [cp$_2$Mo] (cp = η^5-C$_5$H$_5$) was shown to be, along with vanadocene,[5] one of the most versatile metallic carbenes. Its generation may be, however, a crucial point. Displacement of a relatively weakly bonded ligand to the [cp$_2$Mo] moiety may overcome this difficulty and provide a slow reaction producing crystalline materials. Complex [cp$_2$Mo(PhC≡CPh)] (I)[6] has been used as starting material, where the Ph$_2$C$_2$ ligand can be replaced by either formaldehyde or carbon dioxide.

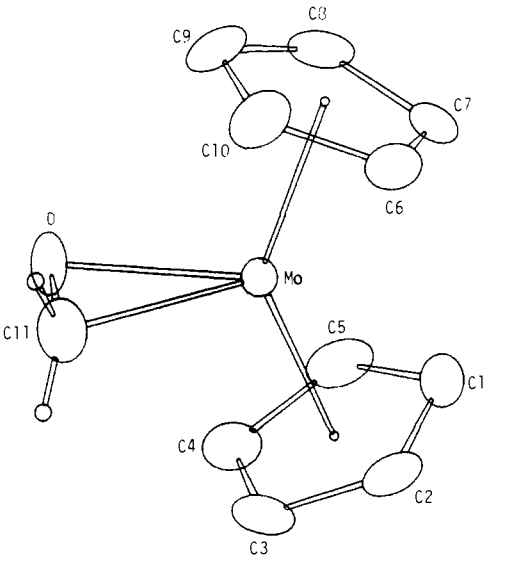


Figure 1. An ORTEP diagram of complex II. Bond lengths (Å) and angles (deg) are the following: C11–O1 = 1.360 (9), Mo–C11 = 2.152 (8), Mo–O = 2.056 (4), cp1–Mo–cp2 = 139.0 (3).

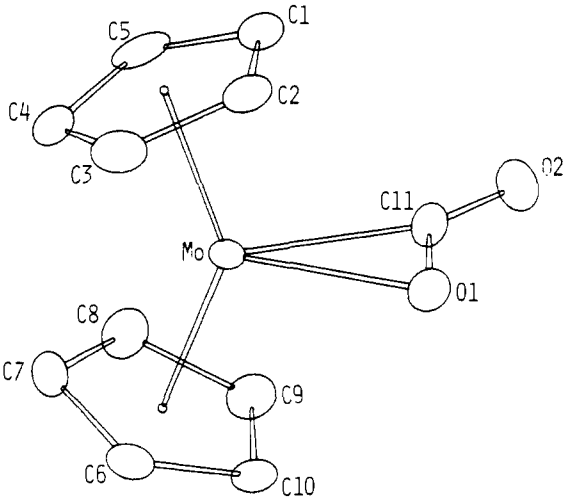
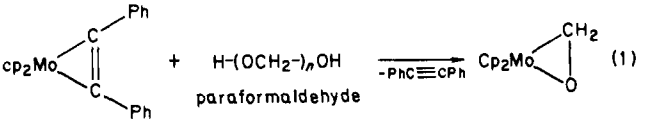


Figure 2. A view of complex III, molecule A. Bond distances (Å) and angles (deg) are the following: Mo–O1, 2.160 (7); Mo–C11, 2.112 (11); C11–O1, 1.288 (14); C11–O2, 1.201 (14); cp1–Mo–cp2, 141.3 (3).

A toluene solution of I was reacted with paraformaldehyde at 80 °C. The suspension was filtered while warm and, on cooling, the resulting solution yielded crystals of II (Figure 1):[7,8]



I II

The structure of II was proven by an X-ray analysis.[9] It is very

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(8) A toluene (50 mL) solution of I (2.09 g) was heated up to 80 °C for 20 min in the presence of an excess of paraformaldehyde. The suspension was filtered while warm, and the resulting solution was cooled to −15 °C. Crystals of II suitable for an X-ray analysis were collected (0.56 g). The unreacted starting material I was recovered from the mother solution by addition of *n*-hexane and cooling. Longer reaction time and higher temperature can increase the yield. Anal. Calcd for $C_{11}H_{12}OMo$: C, 51.58; H, 4.72. Found: C, 51.60; H, 4.72. ν(CO) (Nujol) 1157 vs; ^{1}H NMR spectrum ($CDCl_3$, Me_4Si) δ 3.05 (2 H, s, CH_2), 4.75 (10 H, s, cp); the mass spectrum showed the parent peak at *m/e* 258 and other peaks whose position and intensity are in agreement with the natural isotopic mixture of molybdenum.

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