

Reactivity of the Coordinated Hydroperoxo Ligand

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The reactivity of the hydroperoxo complex $[\text{Co}(\text{CN})_5\text{OOH}]^{3-}$ has been studied in aqueous solution. The complex undergoes acid-catalyzed aquation ($k = 1.89(5) \times 10^{-2} \text{ s}^{-1}$, $\text{p}K_a = 5.21(4)$, $T = 20 \text{ }^\circ\text{C}$, $I = 0.1 \text{ M}$). Assuming an I_d mechanism, this allows the relative affinity for Co(III) to be deduced as $\text{H}_2\text{O}_2 < \text{H}_2\text{O} < \text{HO}_2^-$ and implies H_2O_2 to be a very weak ligand. At neutral pH the hydroperoxo complex effects efficient oxygen atom transfer to L-methionine to give an intermediate identified as $[\text{Co}(\text{CN})_5(\text{L-methionine } S\text{-oxide})]^{2-}$, which then dissociates to $[\text{Co}(\text{CN})_5\text{OH}_2]^{2-}$ and L-methionine *S*-oxide. The reaction is acid catalyzed and is proposed to take place via nucleophilic attack of sulfur on the proximal oxygen of the hydroperoxo ligand with concerted loss of water. The significance of these results for the interaction of hydrogen peroxide with labile metal ions is discussed.

Introduction

Complexes of transition metals with the hydroperoxo ligand, HO_2^- , occupy an unusual position in coordination chemistry. They have been prepared in many different ways: by protonation of peroxo complexes,^{1–3} by insertion of dioxygen into metal–hydrogen bonds,^{4,5} by hydrogen abstraction by metal dioxygen complexes,⁶ by reduction of superoxo complexes,⁷ or simply by the reaction of the metal ion with hydrogen peroxide.^{8–10} Although the complexes have in general been well characterized, there is little structural information and even fewer data on their reactivity. Nevertheless, hydroperoxo complexes are frequently postulated as intermediates in reactions involving dioxygen or hydrogen peroxide, both in catalytic systems^{10,11} and in biological systems.^{12,13} We are thus confronted with a series of complexes which are synthetically accessible by a number of routes, are potentially of great importance as reactive intermediates, yet are poorly understood.

While the absence of information on their chemical behavior is at least partly a consequence of their reactivity, it remains a problem for the assessment of proposed mechanisms for catalytic systems and their optimization.

Some years ago, Bayston and Winfield¹ reported the preparation and isolation of a hydroperoxo complex, pentacyano-(hydroperoxo)cobaltate(III), $[\text{Co}(\text{CN})_5\text{OOH}]^{3-}$ (**1**), as its potassium salt $\text{K}_3[\text{Co}(\text{CN})_5\text{OOH}]$, but limited their studies on the reactivity to the observation that the complex aquated in acidic solution. Pregaglia *et al.*¹⁴ used **1** as a catalyst for oxidation of alkenes but concluded that, in the acetic acid solvent, **1** was not the active oxidizing species. Our attention was drawn to **1** by our observation of its formation during the decomposition of the η^1 -dioxygen complex $[\text{Co}(\text{CN})_5(\text{O}_2)]^{3-}$ in aqueous solution.¹⁵ **1** offers several advantages for studying the reactivity of the coordinated hydroperoxo group: (i) cobalt(III) coordinated to five cyanide ligands may only be reduced with great difficulty, so that there is little chance of the coordinated hydroperoxo group reducing the metal ion; (ii) the cobalt(III) is not readily oxidized, so that redox reactions between the hydroperoxo ligand and the metal ion may be excluded; (iii) the strong binding of cyanide to cobalt excludes the possibility of dissociation of a ligand followed by formation of an η^2 -peroxo complex as observed in the $[\text{Fe}(\text{EDTA})]^-$ system;¹⁶ (iv) the slow kinetics of cobalt(III) substitutions allow classical kinetic methods to be used and offer the possibility of observing intermediate species. In this paper, we report the aquation kinetics of the hydroperoxo complex **1** and the efficient transfer of an oxygen atom from the hydroperoxo ligand to L-methionine.

Experimental Section

Source of Compounds. Unless otherwise stated, compounds used were purchased from Merck or Fluka and were of the highest available purity. $\text{K}_3[\text{Co}(\text{CN})_5\text{OOH}]$ was prepared according to the method of Bayston and Winfield.¹ The dry compound shows little or no decomposition (as shown by the change in its UV spectrum) over a period of weeks if stored below $0 \text{ }^\circ\text{C}$. L-Methionine *S*-oxide was prepared according to the literature.¹⁷ Buffer solutions (lactate, acetate, Tris, phosphate, or borate) were freshly prepared, and ionic strength

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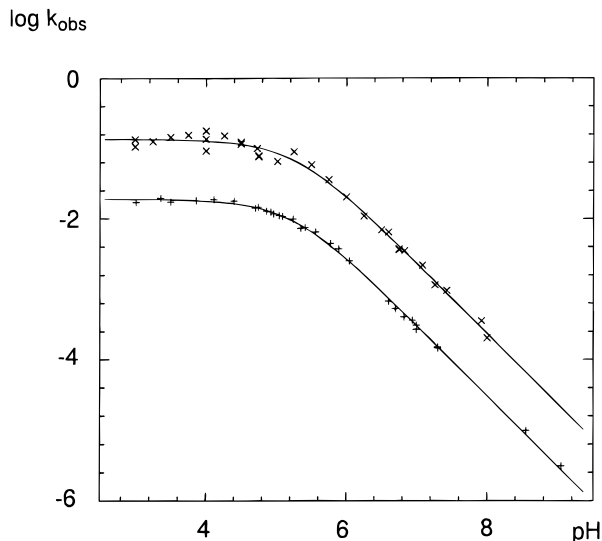


Figure 1. pH dependence of $\log k_{\text{obs}}$ for the aquation of $[\text{Co}(\text{CN})_5\text{OOH}]^{3-}$, **1**, at 20 °C (+) and 40 °C (x). The solid lines are calculated from the least-squares fits of eq 3.

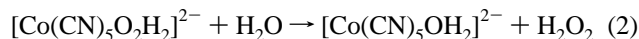
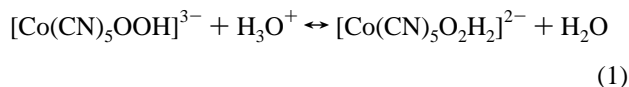
was adjusted to 0.1 M with sodium perchlorate, except for a few measurements with $I = 1$ M.

Kinetic Measurements. Reactions with **1** were carried out by adding small amounts of solid $\text{K}_3[\text{Co}(\text{NC})_5\text{OOH}]$ to a suitably buffered thermostated solution in a spectrophotometer cuvette. The quantity added (typically a few milligrams) was chosen to give an absorbance between 1 and 2 after completion of the mixing. For faster reactions, particularly at 40 °C, slightly more $\text{K}_3[\text{Co}(\text{NC})_5\text{OOH}]$ was added to allow for the significant degree of reaction during mixing and to give a sufficiently large change in absorbance during the observation period. The reaction was followed over at least 3 half-lives by a computer-controlled UV–visible spectrophotometer (Perkin-Elmer Lambda 5), via the disappearance of the 272 nm absorption of **1**. Under the conditions used, the kinetics showed first-order behavior with the exception of certain runs using low methionine concentrations (see below). Observed first-order rate constants were obtained by a standard least-squares fit to the absorbances, and the quality of the fit was assessed by the rms value of the difference between observed and calculated absorbance. This value was typically 0.1% of the total absorbance change during the observation of the kinetics and even for the fastest reactions with half-lives around 5 s was less than 1%. The resulting rate constants were fitted to the rate laws given in the text via a Gauss–Newton nonlinear least-squares program which minimized $\sum\{\ln(k_{\text{obs}}/k_{\text{calc}})\}^2$. The fits were regarded as satisfactory when the rms value of $\ln(k_{\text{obs}}/k_{\text{calc}})$ was comparable with experimental errors, and no systematic deviations of k_{obs} from k_{calc} were observed. The reaction of hydrogen peroxide with L-methionine was studied by adding 5 μL of H_2O_2 (30%) to a thermostated spectrophotometer cuvette containing L-methionine and a suitable buffer solution and by following the decrease in absorbance at 255 nm.

Analysis. The formation of the cobalt pentacyano aquo complex was confirmed by UV–visible spectroscopy.¹⁸ The unreacted methionine and methionine sulfoxide were identified by thin-layer chromatography. The solvent used was a 1-butanol–acetic acid–water mixture, in 4:1:5 (v/v) ratio. Spots were developed by spraying the plate with 0.2% ninhydrin solution, followed by heating the plate at 100 °C in an oven for 3–4 min. The reaction mixture was analyzed on Beckman amino acid analyzer, Model 119 CL, with a sulfonated cation-exchange column for 96 min, and the detection limit was 10 nmol after postcolumn derivatization with ninhydrin.¹⁹ The instrument was calibrated with a standard mixture of amino acids before each run.

Results

Aquation of $[\text{Co}(\text{CN})_5\text{OOH}]^{3-}$. The ion $[\text{Co}(\text{CN})_5\text{OOH}]^{3-}$ aquates cleanly to $[\text{Co}(\text{CN})_5\text{OH}_2]^{2-}$ (identified by its electronic spectrum¹⁸) and hydrogen peroxide (identified by iodometric titration¹⁵). The kinetics are first order in cobalt but depend strongly on the pH of the solution (Figure 1). This dependence is typical of an acid-catalyzed substitution reaction.²⁰ Assuming an initial protonation equilibrium followed by dissociation



one may derive the rate law as

$$\frac{-d[\text{Co}]}{dt} = k_{\text{obs}}[\text{Co}] = \frac{k_2 K_1 [\text{Co}][\text{H}_3\text{O}^+]}{1 + K_1 [\text{H}_3\text{O}^+]} \quad (3)$$

where $[\text{Co}]$ is the total concentration of protonated and non-protonated forms of **1**. This expression was fitted to the observed first-order rate constants, k_{obs} . As shown in Figure 1, the fit is satisfactory over the whole range studied. The derived rate constants, k_2 , are given in Table 1; the values for K_1 were identical within experimental error at the two temperatures studied (20 and 40 °C): $\log K_1(20 \text{ °C}) = 5.21(2)$, $\log K_1(40 \text{ °C}) = 5.24(3)$. Figure 1 shows no indication of a leveling out in the rate at high pH, and we have therefore assumed the aquation of the unprotonated complex to be negligible; this gives an upper limit for the rate of this reaction as $5 \times 10^{-6} \text{ s}^{-1}$ at 20 °C, implying the acid-catalyzed pathway to be at least 10^3 times faster than the noncatalyzed pathway. Such an acceleration is consistent with the factor of 5800 observed for the acid catalysis of aquation of $[\text{Co}(\text{CN})_5\text{N}_3]^{3-}$ ²¹ and the observation that the hydroxo complex $[\text{Co}(\text{CN})_5\text{OH}]^{3-}$ is inert compared to the protonated aquo complex.²²

The kinetics of aquation are not sensitive to the buffer media but in the pH range 6.5–8 are sensitive to ionic strength: studies with ionic strength maintained at 1 M gave a rate law of the form $k'[\text{Co}][\text{H}^+]$ with k' reduced by a factor of 7.5 compared to the values obtained with an ionic strength of 0.1 mol/L. Since in this range $k' \approx k_2 K_1$, and k_2 is not expected to be strongly dependent on ionic strength,²³ we associate this decrease with a decrease in K_1 in solutions of high ionic strength, which is reasonable given the high charge of **1**.

Oxidation of Methionine. Metal hydroperoxo complexes are potential oxygen atom transfer agents, and the possibility that oxygen atom transfer could compete with aquation of complex **1** was therefore investigated. Edwards has investigated oxygen atom transfer from hydrogen peroxide to sulfur in some detail,²⁴ and to compare the efficiency of hydrogen peroxide and metal-bound hydroperoxide, we chose L-methionine as a convenient water-soluble substrate. The reaction of L-methionine with free hydrogen peroxide was found to obey the following

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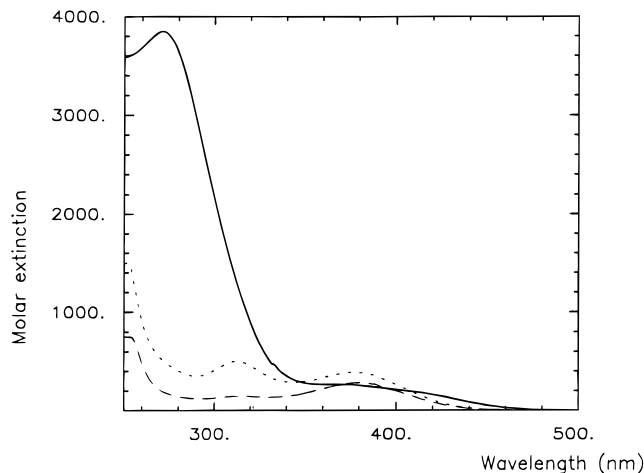


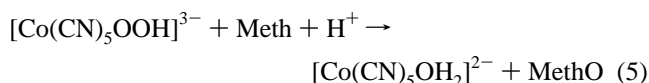
Figure 2. Absorption spectra of **1** (—), the intermediate formed on reaction with methionine (···), and $[\text{Co}(\text{CN})_5\text{OH}_2]^{2-}$ (---).

rate law:

$$-\frac{d[\text{H}_2\text{O}_2]}{dt} = k_4[\text{H}_2\text{O}_2][\text{methionine}] \quad (4)$$

with $k_4 = 5.6(2) \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ (20 °C, $I = 0.1\text{M}$), about twice as fast as observed for thioxane at 25 °C by Edwards et al.²⁴ No dependence upon pH was observed in the pH range 5.9–6.8. Edwards²⁴ observed an acid-catalyzed pathway to be important only at $\text{pH} < 3$.

The addition of $\text{K}_3[\text{Co}(\text{CN})_5\text{OOH}]$ to a solution of L-methionine (Meth) buffered at neutral pH with phosphate results in the disappearance of the 272 nm band of the hydroperoxo complex at a rate appreciably greater than that observed for simple aquation. The initial product of the reaction, X, shows an absorption maximum at 314 nm (Figure 2), which, over a period of a few hours, diminishes to give the spectrum of the aquo complex $[\text{Co}(\text{CN})_5\text{OH}_2]^{2-}$. Analysis by chromatography showed clearly the formation of L-methionine S-oxide (MethO) in the final solution. No other products of oxidation were observed, and in particular the amino acid analysis showed no trace of methionine sulfone. The stoichiometry of the reaction is thus



Given that the reaction with L-methionine is much faster than both the aquation and the reaction of free hydrogen peroxide with L-methionine, we can exclude an initial dissociation of hydrogen peroxide followed by reaction of L-methionine with free hydrogen peroxide. The reaction must therefore involve attack by methionine on the hydroperoxo complex, leading to the intermediate X. The most plausible composition for X is L-methionine S-oxide complexed to a $[\text{Co}(\text{CN})_5]^{2-}$ moiety, $[\text{Co}(\text{CN})_5(\text{MethO})]^{2-}$. Extensive efforts to isolate X were unsuccessful, and we base this assignment on the following points:

(a) The intensity and energy of the absorption band of X at 314 nm are consistent with a MLCT band from cobalt to the $\text{S}=\text{O} \pi^*$ orbital, as has been observed in other cases where an unsaturated ligand is bound²⁵ (or is thought to be bound²⁶) to $[\text{Co}(\text{CN})_5]^{2-}$.

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(26) Treatment of a solution of $\text{K}_3[\text{Co}(\text{CN})_5\text{OOH}]$ in DMSO with anhydrous trifluoromethanesulfonic acid gave a solution showing an absorption at 310 nm; since the expected product of this reaction is $[\text{Co}(\text{CN})_5\text{OS}(\text{CH}_3)_2]^{2-}$, it seems reasonable to assign the band of compound X to a $\text{Co} \rightarrow \text{O}=\text{S}$ charge transfer.

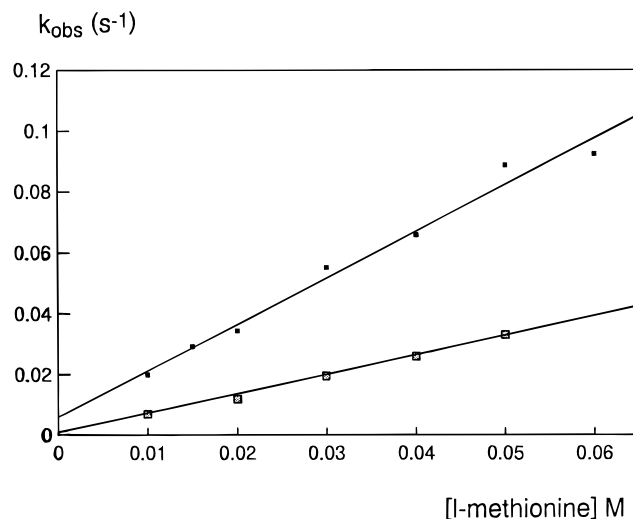


Figure 3. Dependence of the observed rate constants for disappearance of **1** on L-methionine concentration at pH 7.0 (■) and pH 7.5 (□).

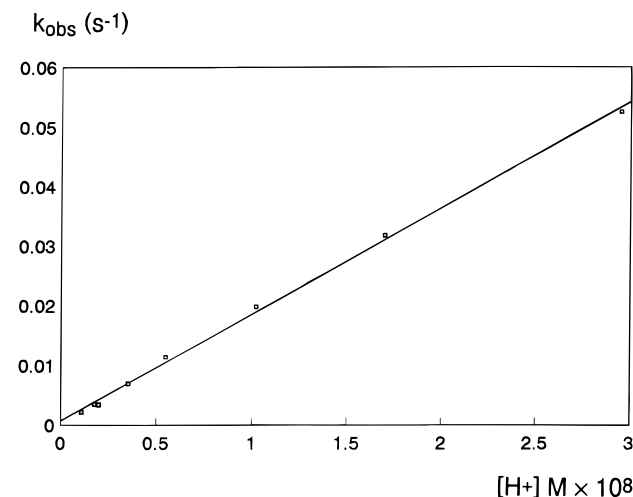
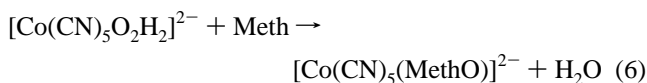


Figure 4. Dependence of the observed rate constant for disappearance of **1** on hydrogen ion concentration for $[\text{L-methionine}] = 0.01 \text{ M}$.

(b) $[\text{Co}(\text{CN})_5(\text{MethO})]^{2-}$ would be expected to aquate to $[\text{Co}(\text{CN})_5(\text{OH}_2)]^{2-}$ and MethO at a rate similar to that observed for water exchange in $[\text{Co}(\text{CN})_5(\text{OH}_2)]^{2-}$ which has a half-life of about 40 min at 20 °C.²³

(c) The product is also consistent with the mechanism proposed from the kinetic data (vide infra).

The kinetics of the reaction have been studied at 20 °C ($I = 0.1 \text{ M}$) by following the disappearance of the 272 nm band of **1** in the range pH 6–8 with methionine concentrations between 0.01 and 0.06 M. The pseudo first order rate constants depend linearly on the methionine concentration (Figure 3), and hydrogen ion concentration (Figure 4). These results are typical of an acid-catalyzed reaction as observed for the aquation of the hydroperoxo complex, and we assume a two-step mechanism involving an initial protonation step (eq 1) followed by



Under experimental conditions, the rate of the aquation reaction was always less than 2% of the rate for reaction with methionine. It was therefore neglected in the treatment of the data, and the observed rate constants for the disappearance of the band at 272 nm were fitted to the equation

$$-\frac{d[\text{Co}]}{dt} = k_{\text{obs}}[\text{Co}] = k_6[\text{Meth}] \left\{ \frac{K_1[\text{H}_3\text{O}^+]}{1 + K_1[\text{H}_3\text{O}^+]} \right\} [\text{Co}] \quad (7)$$

where K_1 is the protonation constant for aquation obtained above (eq 1). A good fit for all data was obtained with $k_6 = 1.18(8) \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$. The inclusion of an uncatalyzed pathway involving direct attack of L-methionine on unprotonated **1** did not significantly improve the fit, and the rate constant obtained for the uncatalyzed pathway ($7 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$) was of a magnitude comparable to that of its estimated standard deviation; we therefore consider it to be negligible. Equation 7 requires that the rate of oxidation of methionine should attain a limiting value at low pH values, as observed for the acid-catalyzed aquation. To observe this while maintaining the kinetics in an experimentally accessible range, it is necessary to use low methionine concentrations. This has two disadvantages: the oxygen atom transfer is now of a rate comparable to that of the aquation (and the reaction can no longer be followed by observation at one wavelength), and the conditions for pseudo-first-order kinetics are no longer satisfied. A number of runs were made with a methionine concentration of 10^{-3} M and showed that the rate did indeed tend to a limit at low pH, but the kinetics were clearly no longer well described by a simple first-order treatment, and these runs were excluded from the mathematical treatment; these results may thus be regarded only as qualitative support for the mechanism.

Reactions with Other Substrates. The reactions of **1** with other potential oxygen acceptors were studied briefly at pH 7. L-Cysteine reacts similarly to methionine as far as spectral changes are concerned with a new band appearing at 310 nm and then disappearing with time. The isolated organic product from this reaction appeared to be cystine *S*-oxide, implying that further reaction had taken place. Since cysteine is also a potential one-electron reductant and since the reaction appeared to be less clean, this reaction was not investigated in detail. In the presence of allylglycine or allyl alcohol the 272 nm band of **1** disappeared at the rate expected for aquation reaction, and consequently oxygen atom transfer to these substrates does not appear to take place.

Discussion

Table 1 gives the rate constants for aquation together with data from the literature for other aquation reactions of $[\text{Co}(\text{CN})_5\text{X}]^{n-}$ species which have been established to take place by I_d mechanisms.^{22,23} Our results show that H_2O_2 coordinated to $[\text{Co}(\text{CN})_5]^{2-}$ is appreciably more labile than water in $[\text{Co}(\text{CN})_5\text{OH}_2]^{2-}$;²³ the upper limit for the rate constant for the uncatalyzed aquation of $[\text{Co}(\text{CN})_5\text{OOH}]^{3-}$ is much lower than that for water substitution, clearly establishing the lower lability of the hydroperoxo ligand. The estimated enthalpy of activation of ca. 70 kJ mol^{-1} for the aquation of $[\text{Co}(\text{CN})_5\text{O}_2\text{H}_2]^{2-}$ is, as expected, lower than the 90 kJ mol^{-1} reported for $[\text{Co}(\text{CN})_5\text{OH}_2]^{2-}$.²³ The greater lability of hydrogen peroxide when compared to water has previously been observed for hydrogen peroxide bound to $[\text{Cr}(\text{OH}_2)_5]^{3+}$,²⁷ which is several hundred times more labile than water bound to the same moiety.²⁸

Given the I_d mechanism of aquation, it is reasonable to assume a linear free energy relationship between lability and the stability of the complex.²⁹ Since, as Taube remarked some

Table 1. Kinetic Data for the Aquation Reactions of $[\text{Co}(\text{CN})_5\text{X}]^{n-}$

X	$k \text{ (s}^{-1}\text{)}$		ionic strength (M)	ref
	20 °C	40 °C		
H_2O_2	$1.89(5) \times 10^{-2}$	$1.35(6) \times 10^{-1}$	0.10	this work
HO_2^-	$<5 \times 10^{-6}$	$<10^{-4}$	0.10	this work
H_2O	3.12×10^{-4}	3.5×10^{-3}	0.35	23
N_3H		3.2×10^{-3}	1.0	21
N_3^-		5.5×10^{-7}	1.0	21

years ago,³⁰ there is very little information on the stabilities of peroxide complexes, it is interesting to use the kinetic data to assess the relative thermodynamic stabilities of aqua and hydroperoxo complexes. Our results show clearly the stability order $\text{H}_2\text{O}_2 < \text{H}_2\text{O} < \text{HO}_2^-$, and this agrees both with the basicity of H_2O_2 being lower than water,³¹ and with the data available for the $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ system.³² This leads to the important conclusion that complexes of H_2O_2 will be thermodynamically unstable to aquation unless the hydrogen peroxide is deprotonated to give a hydroperoxo ligand. The stability of hydroperoxo complexes will thus depend very strongly on the pH of the medium and upon the $\text{p}K_a$ of the coordinated hydroperoxo ligand. Although the existence of these protonation equilibria has frequently been mentioned in the literature, the possibility that they might dramatically affect the stability of the complex has not, to our knowledge, been considered in any detail. The $\text{p}K_a$ observed for $[\text{Co}(\text{CN})_5\text{O}_2\text{H}_2]^{2-}$, 5.2, is roughly 5 log units lower than the value of 10.5 reported for $[\text{Co}(\text{CN})_5\text{OH}_2]^{2-}$;³³ this difference is slightly greater than the difference of 3.7 log units between free H_2O_2 and water.³¹ The only other value of which we are aware is that for Fe^{3+} , for which coordinated hydrogen peroxide was reported to be roughly 30 times more acid than coordinated water,^{30,32} although these values were obtained in a mixture of water and hydrogen peroxide, which may not be directly comparable with an aqueous solution. In the absence of better data, it would seem reasonable to assume that the $\text{p}K_a$ of the coordinated hydrogen peroxide ligand will be 2–5 units lower than that of coordinated water. Thus the complex reported to be formed by reaction of H_2O_2 with [5,10,15,20-tetrakis(2,6-dichloro-3-sulfonatophenyl)porphyrinato]iron(III), for which the $\text{p}K_a$ of coordinated water has been measured to be 7.85,³⁴ is almost certainly a hydroperoxo complex at neutral pH.

The acid catalysis observed for the decomposition of the hydroperoxo complex is a natural consequence of the relative weakness of hydrogen peroxide as a ligand. Acid catalysis has also been observed for $[\text{Co}(\text{CN})_5\text{N}_3]^{3-}$ by Haim and Wilmarth.²¹ In the case of $[\text{Co}(\text{CN})_5\text{OOH}]^{3-}$, it is interesting to consider the site of protonation: the two possible sites are shown in Scheme 1.

The kinetic data presented here give only the macroscopic protonation constant and cannot distinguish between the two protonation sites or give a value for the dimensionless constant K_8 . Similarly the rate constants involving the protonated complex, k_2 and k_6 , are macroscopic. It is however obvious from the principle of least motion that the proximal form **3** is a more favorable precursor for dissociation than the ylidic, distal form **2**, and that it is more likely to weaken the Co–O bond.

The reaction of $[\text{Co}(\text{CN})_5\text{OOH}]^{3-}$ with methionine to give methionine *S*-oxide shows that hydroperoxo complexes can act as efficient oxygen atom transfer agents. Such behavior has

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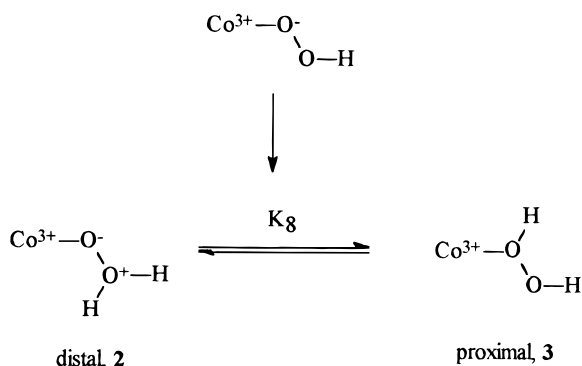
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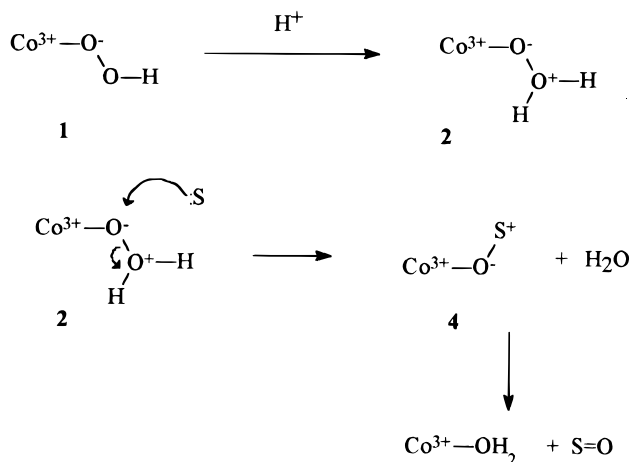
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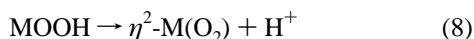
Scheme 1



Scheme 2



previously been noted for a (μ -hydroperoxy)dycopper(II) complex by Karlin and co-workers,² who reported efficient oxygen atom transfer to triphenylphosphine, while the unprotonated peroxy complex reacted with triphenylphosphine to give dioxygen and a (triphenylphosphine)copper(I) complex. It may be noted at this point that peroxy complexes of the later transition metals are generally nucleophilic³⁵ and will not transfer oxygen atoms to basic substrates. Thus the possible second deprotonation step

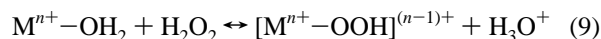


will in general deactivate the dioxygen moiety for atom transfer reactions. The formation of an η^2 -peroxy species has been established in the reaction of hydrogen peroxide with $[\text{Fe}(\text{EDTA})]^-$ ³⁶ either giving a seven-coordinate complex or involving the dissociation of a carboxylate group,¹⁶ but this is unlikely for $[\text{Co}(\text{CN})_5\text{OOH}]^{3-}$ given the preference of cobalt(III) for octahedral geometry and the kinetic and thermodynamic stability of the Co-CN bond.

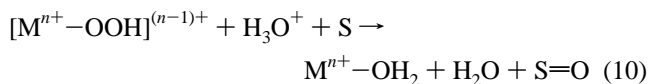
Under the conditions studied, $[\text{Co}(\text{CN})_5\text{OOH}]^{3-}$ reacts with L-methionine 2×10^4 times faster than free hydrogen peroxide. The reaction of sulfides with H_2O_2 is known to be acid catalyzed at low pH²⁴, and it is reasonable to assume that $[\text{Co}(\text{CN})_5\text{OOH}]^{3-}$ is more reactive at neutral pH by virtue of its greater basicity. The mechanism proposed for the reaction is given in Scheme 2. This mechanism accounts for the observed acid catalysis which allows the O-O bond to be broken with loss of water rather than hydroxide and accounts for the observation of the

intermediate X which is identified as a L-methionine S-oxide complex, **4**. An attack by the substrate S on the distal oxygen atom would inevitably lead to heterolytic O-O bond cleavage and direct formation of a $[\text{Co}(\text{CN})_5\text{OH}_2]^{2-}$ species rather than an intermediate and may thus be excluded. The distally protonated intermediate **2** is clearly, by the principle of least motion, a more favorable intermediate than the proximally protonated intermediate **3**. The fact that the bimolecular oxygen atom transfer reaction is able to compete successfully with the unimolecular aquation reaction may be an indication that the value of K_8 is much less than 1. Theoretical calculations on oxygen atom transfer reactions of hydrogen peroxide have recently established the need for a 1,2-hydrogen shift before oxygen atom transfer from H_2O_2 and have shown that this results in a high kinetic barrier in the absence of protic solvent catalysis.³⁷ A distally protonated hydroperoxy complex as proposed here offers an obviously favorable intermediate for oxygen atom transfer. Experiments to determine the importance of general-acid catalysis for oxygen atom transfer are currently in progress. In biological systems oxygen atom transfer might be favored over aquation by suitable hydrogen-bonding interactions which would stabilize distal protonation.

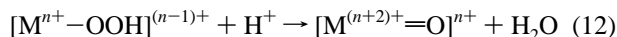
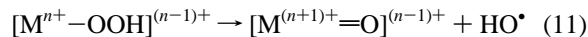
The experiments reported here have concerned the kinetically inert cobalt(III) ion, and this has allowed us to follow the kinetics by classical methods and to observe an intermediate in the atom transfer reaction. We may briefly consider the implications for oxidations by hydrogen peroxide catalyzed by labile metal ions. The first step will be



Given that free hydrogen peroxide is a poorer ligand than water, which is generally present at much higher concentrations, we may exclude the formation of $\text{M}^{n+}\text{-O}_2\text{H}_2$. This reaction will reach equilibrium if M^{n+} is labile, and the concentration of $[\text{M}^{n+}\text{-OOH}]^{(n-1)+}$ will be inversely dependent upon the acidity of the solution. If oxygen transfer takes place, the second step will be



Alternatively the metal ion can reduce the coordinated hydroperoxy ligand by a one- or two-electron process to give new oxidizing species:¹⁰



Both reactions 10 and 12 involve heterolytic breakage of the O-O bond and will probably involve acid catalysis; however, the initial equilibrium (9) is inversely dependent on the proton concentration, and consequently the overall reaction rate may appear to be acid independent. In strongly acid solution, equilibrium 9 is extremely unfavorable but radical production by reduction of noncoordinated hydrogen peroxide by the metal is still possible:



In support of this, it has been observed in the $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ system that low pH favors production of the hydroxyl radical (presum-

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ably by reaction 13), while higher pH and high concentrations of H_2O_2 (which would favor equilibrium 9) increase the yield of the ferryl ($\text{Fe}^{\text{IV}}=\text{O}$) species (reaction 12), which must take place via an inner-sphere mechanism. Finally, we should note that the relative binding strengths of HO_2^- and HO^- remain to be assessed. Since HO^- is a stronger base than HO_2^- , it may well be a better ligand, in which case the formation of hydroperoxo complexes would only be favorable at pH values below the $\text{p}K_{\text{a}}$ of coordinated water.

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Supporting Information Available: Tables of observed rate constants (2 pages). Ordering information is given on any current masthead page.

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