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Effect of pH on the Kinetics and Thermodynamics of Oxygen Coordination to a Macrocyclic Cobalt(II) Complex

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The macrocyclic cobalt(II) complex $Co(hmc)(H_2O)_2^{2+}$ (hmc = *C-meso*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane) forms $Co(hmc)(OH)O_2^+$ in reaction with O_2 in aqueous solution at pH >7. The kinetics of oxygen binding in moderately alkaline media remain essentially the same as measured previously below pH 7, but the rate constant decreases by a factor of 5 at high pH where $Co(hmc)(H_2O)_2^{2+}$ deprotonates ($pK_a = 11.68$). The increase in pH has a much more dramatic effect on the rate constant for oxygen dissociation, with k_h for $Co(hmc)(OH)O_2^+$ ($\sim 0.021\ s^{-1}$) being 10^6 times lower than that for the aqua form $Co(hmc)(H_2O)O_2^{2+}$. The two forms are related by a pK_a of 6.42. Oxygen dissociates from $Co(hmc)(SCN)O_2^+$ with a rate constant of 17.7 s^{-1}. As a result of the low oxygen dissociation rates, the equilibrium constants for O_2 binding by thiocyanato and hydroxo complexes are much larger than that for the aqua complex.

Introduction

Oxygen complexes of iron and cobalt have received a lot of attention in the design of synthetic oxygen carriers. Iron is an obvious choice because of its presence at the active sites of naturally occurring oxygen carriers. In many cases, however, oxygen complexes of cobalt are excellent models for metal–dioxygen binding[1–3] since ligand oxidation by the MO_2 complex seems to be less of a problem than with the synthetic iron compounds.

The reaction of cobalt(II) complexes with O_2 often takes place according to the two-step scheme of eqs 1 and 2.[1–5] The assignment of the whole number oxidation states is only an approximation, and the extent of electron transfer in these reactions has been a subject of much debate.[1,4,6]

$$Co^{II} + O_2 \rightleftarrows Co^{III}O_2 \qquad (1)$$

$$Co^{III}O_2 + Co^{II} \rightleftarrows Co^{III}O_2Co^{III} \qquad (2)$$

The tendency of cobalt(II) complexes to form 1:1 adducts with O_2 increases[1] in nonaqueous solvents at low temperatures and low concentrations and in the presence of Lewis bases. Reports concerning the 1:1 cobalt–oxygen adducts in water at ambient conditions are relatively rare.[1,7–13] As expected, the steric bulk of the ligands favors the formation of the 1:1 complexes in both aqueous and nonaqueous systems. As an example, two macrocyclic cobalt(II) complexes, $Co(cyclam)(H_2O)_2^{2+}$ (cyclam = 1,4,8,11-tetraazacyclotetradecane) and $Co(hmc)(H_2O)_2^{2+}$ (hmc = *C-meso*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane), can be compared in aqueous solution. (With some obvious exceptions the coordinated molecules of H_2O will be omitted hereafter.) At equilibrium with 1 atm of O_2 a significant portion of the cobalt cyclam exists as the μ-peroxo dimer $\{Co(cyclam)\}_2O_2^{4+}$.[14] In contrast, the sterically crowded $Co(hmc)^{2+}$ participates only in reaction 1, with $k_1 = 5 \times 10^6\ M^{-1}\ s^{-1}$ and $k_{-1} = 1.7 \times 10^4\ s^{-1}$, reaction 2 being negligible.[11] Moreover, in the presence of coordinating anions the rate constants for the binding of O_2 remain nearly independent of the nature of the axial ligand (H_2O, Cl^-, SCN^-), but the kinetics of release of O_2 are dramatically influenced by the ligand.[12] In an attempt to understand the exact role of axial ligands we originally set up to examine the effect of pyridine (py) and imidazole (im) on the kinetics and thermodynamics of O_2 binding by $Co(hmc)^{2+}$, eq 3 (L = py, im). The strong Lewis basicity of py and im might be expected to influence the reverse reaction even more than SCN^- and Cl^- do, but charge consideration would seem to favor stronger O_2 binding for the chloro and thiocyanato complexes.

$$Co(hmc)L^{2+} + O_2 \rightleftarrows LCo(hmc)O_2^{2+} \quad k_f, k_h \qquad (3)$$

We have found, quite unexpectedly, that py and im do not form complexes with either $Co(hmc)(H_2O)_2^{2+}$ or its O_2 adduct. Nonetheless, both bases still have an effect on the kinetics and thermodynamics of O_2 binding to $Co(hmc)(H_2O)_2^{2+}$. This effect, traced to the Bronsted basicity of the bases, appeared sufficiently interesting in its own right that we undertook a complete study of the effect of pH on O_2 binding by $Co(hmc)(H_2O)_2^{2+}$.

We have also measured directly the rate constant for homolysis (oxygen release) of $Co(hmc)(NCS)O_2^+$. Only an upper limit for k_h was reported previously.[11]

Experimental Section

The solvent used throughout was distilled water purified by passage through a Milli-Q Millipore system. The macrocyclic ligand hmc, its cobalt(II) complex, and the methylcobalt(III) complex *trans*-$Co(hmc)(H_2O)(CH_3)(CF_3SO_3)_2$[15] were prepared as described previously.[11] Trifluoromethanesulfonic acid, CF_3SO_3H, 98% (Aldrich), was purified by vacuum distillation and diluted as needed. Pyridine, NaSCN (Fisher, Certified ACS), imidazole, 1-methylimidazole, and *tert*-butyl hydroperoxide (all Aldrich analyzed) were used without purification. The salt $(NH_4)_2ABTS$, where $ABTS^{2-}$ = 2,2′-azino bis(3-ethylbenzthiazoline-

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6-disulfonate), was used as purchased from Sigma. Stock solutions of $ABTS^{\bullet-}$ were prepared by oxidation of $ABTS^{2-}$ by Br_2.[16] The resulting solutions were thoroughly purged with an appropriate gas (Ar, air, or O_2) to remove the slight excess of bromine. The concentrations of diluted solutions of the reagents were determined spectrophotometrically: $Co(hmc)^{2+}$, $\epsilon_{480} = 70\ M^{-1}\ cm^{-1}$;[11] $ABTS^{\bullet-}$, $\epsilon_{650} = 1.2 \times 10^4\ M^{-1}\ cm^{-1}$.[17]

Spectrophotometric measurements were done by the use of a Cary 219 and Perkin-Elmer diode array 3840 spectrophotometers.

The kinetics of the formation of cobalt–oxygen adducts were studied as described earlier[11] by use of a laser flash photolysis system with LD 490 dye (Exciton).[18] Solutions of the $Co–O_2$ adduct (2×10^{-4} M) were flash-photolyzed to generate O_2-free complex. The subsequent buildup of the oxygen adduct in O_2-containing solutions was monitored at 360 nm, the wavelength with the best signal to noise ratio.

Laser flash photolysis was used to measure the rate constant for the reaction of $Co(hmc)(SCN)^+$ with $ABTS^{\bullet-}$. The initial concentrations of $Co(hmc)(CH_3)^{2+}$, 2×10^{-4} M; SCN^-, 0.1 M; and O_2, 2.6×10^{-4} M, were held constant whereas variation of $[ABTS^{\bullet-}]$, initially 1×10^{-4} M, was provided by its slow decay in the reaction with SCN^-. The $ABTS^{\bullet-}$ absorption at 650 nm was used to watch its decay and to calculate its average concentration during every run.

The oxidation of $Co(hmc)^{2+}$ by $ABTS^{\bullet-}$ in the presence of Lewis bases was monitored under O_2-free conditions by use of a Canterbury SF-3A stopped-flow spectrophotometer and an OLIS 3820 kinetic data system. The total concentration of cobalt was held between 3 and 15 μM. The absorption maximum of $ABTS^{\bullet-}$ at 415 nm ($\epsilon = 3.5 \times 10^4\ L\ mol^{-1}\ cm^{-1}$) was used to follow the kinetics of its reactions with Co(II) complexes. Most of the kinetic data for the homolysis of cobalt–oxygen adducts were obtained with $ABTS^{\bullet-}$ as scavenger for the cobalt(II) released. The kinetic measurements with *tert*-butyl hydroperoxide (0.75–100 mM) as scavenger for cobalt(II) were carried out by use of a Cary 219 spectrophotometer.

The kinetic and equilibrium experiments were carried out at an ionic strength defined by the complex ($<1 \times 10^{-3}$ M) or by the concentrations of NaSCN, NaOH, or buffer system used.[19] The temperature was controlled in all the measurements at 25 ± 0.5 °C. The concentration of O_2 was varied by combining aqueous solutions saturated at 25 °C with oxygen, air, and argon. The solubility of O_2 in H_2O was taken as 1.27 mM and interpolated for 0.1 M NaSCN as 1.24 mM.[20]

Results

Preliminary Observations. The interaction of several Lewis bases with $Co(hmc)^{2+}$ in deaerated solution has been checked by UV–visible spectroscopy. No spectral changes other than those caused by dilution were observed upon addition of up to 0.1 M py, im, or 1-methylimidazole (1-Meim) to a 5 mM solution of $Co(hmc)^{2+}$. Also, after the base was neutralized with acid, no spectral change was seen. These observations indicate either that the coordination of pyridine and imidazoles does not take place or that the accompanying absorbance changes are too small to observe. In the next experiment up to 1 M py or im was added to a solution containing 0.5 mM $Co(hmc)^{2+}$ and 0.4 mM $Co(hmc)(SCN)^+$ (7.5 mM total SCN^-). No spectral changes were observed except those caused by dilution and absorption of the base. Thus neither py nor im can compete with thiocyanate which binds to $Co(hmc)^{2+}$ with $K_{SCN} = 174$.[12] The enhanced formation of the $Co–O_2$ adduct in the presence of Lewis bases must therefore be simply a pH effect. This was further demonstrated by the kinetic studies (see later) with all the kinetic data forming a self-consistent picture irrespective of whether py/CF_3SO_3H, py, im, 1-Meim, or OH^- were used to adjust the pH.

Acidic aqueous solutions of $Co(hmc)^{2+}$ saturated with O_2 exhibited significant absorbance in the near-UV region, characteristic of the cobalt(II)–oxygen adduct. The spectrum showed a maximum at 333 nm, consistent with that reported previously.[11] At pH 5–13, adjusted with py, im, 1-Meim, or OH^-, the absorbance at the ~320 nm maximum was even larger and similar to that observed in SCN^- solutions,[12] indicating that under these conditions almost all the cobalt was present as the oxygen adduct. This was confirmed by varying the pH and $[O_2]$, see later.

The cobalt–oxygen adduct decomposes irreversibly in a reaction that was found to be faster at higher pH and lower $[O_2]$. The loss of absorbance of $Co–O_2$ was recorded at 320 nm for initial cobalt and oxygen concentrations of $\sim 2.5 \times 10^{-4}$ M (O_2 in a 5–10% excess) at pH 9–10. The decay followed first-order kinetics for up to 2 half-lives yielding a rate constant of $\sim 1.2 \times 10^{-3}\ s^{-1}$. This is much slower than the reaction of interest, the homolytic cleavage of the $Co–O_2$ bond. The UV–visible spectra of the decomposed solutions of $Co–O_2$ resembled those obtained by oxidation of $Co(hmc)^{2+}$ with hydrogen peroxide and indicated that both types of reactions yielded Co(III) products.

Kinetics of the Formation and Homolysis of $Co(hmc)L^{n+}–O_2$ Adducts ($L = H_2O, OH^-, SCN^-$). The photochemical behavior of the solutions containing $Co(hmc)^{2+}$ and O_2 at pH 5–13 in the laser kinetic experiments was qualitatively the same as previously observed at pH <7.[12] After the bleach in the flash, the absorbance at 360 nm returned exactly to the preflash value, indicating that the same oxygen adduct was first photohomolyzed and then subsequently reconstituted in a dark reaction. Owing to the less favorable absorbance changes at the pH used in this work at both the analytical and irradiation wavelengths, as well as the possibly lower quantum yields of Co(II),[21] the laser kinetic experiments required the use of relatively large cobalt concentrations, comparable to the lowest $[O_2]$.[22]

The data obeyed the rate law of eq 4 (Figure 1), where k_f^{app} and k_h^{app} are the respective acid-dependent rate constants for the formation and homolysis of the $Co–O_2$ adducts. The initial and

$$k_{obs} = k_f^{app}\{[Co(hmc)L^{n+}]_{eq} + [O_2]_{eq}\} + k_h^{app} \qquad (4)$$

final absorbances at 360 nm were used to calculate the equilibrium concentrations of all the components in individual runs. The values of k_f^{app} are summarized in Table I.

The term k_h^{app} (intercept in Figure 1) was negligible in comparison with the observed rate constants. To obtain the kinetic data for homolysis, a series of scavenging experiments was designed according to eqs −3 and 5, where Sv represents a scavenger. A

$$Co(hmc)L^{n+} + Sv \xrightarrow{k_{Sv}} \text{products} \qquad (5)$$

steady-state approximation for $Co(hmc)L^{n+}$ yields the rate law in eqs 6 and 7. The possibility of scavenging the other homolysis

$$\frac{dP}{dt} = k_{obs}[CoO_2^{\ n+}] \qquad (6)$$

$$k_{obs} = \frac{k_h^{app}k_{Sv}[Sv]}{k_f^{app}[O_2] + k_{Sv}[Sv]} \qquad (7)$$

product, dioxygen, was less attractive not only because an effective O_2 scavenger would be more difficult to find but also because

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(19) The binding of O_2 to $Co(hmc)^{2+}$ was found to be independent of ionic strength in the range 0.001–1 M.[12]

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(22) The absorbance changes at 320 nm are in fact better at pH >7 than they were[11,12] in acidic solutions, but in the laser-flash photolysis measurements this wavelength is not accessible to us. In order to obtain larger absorbance changes, an excess of $Co(hmc)L^{2+}$ was used in some experiments. However, the exceptionally fast decomposition of the oxygen adduct under those conditions precluded acquisition of useful kinetic data.

(23) The $Co(hmc)^{3+/2+}$ couple exhibits $E° = 0.592$ V vs NHE (Liteplo, M. P.; Endicott, J. F. *Inorg. Chem.* **1971**, *10*, 1420).

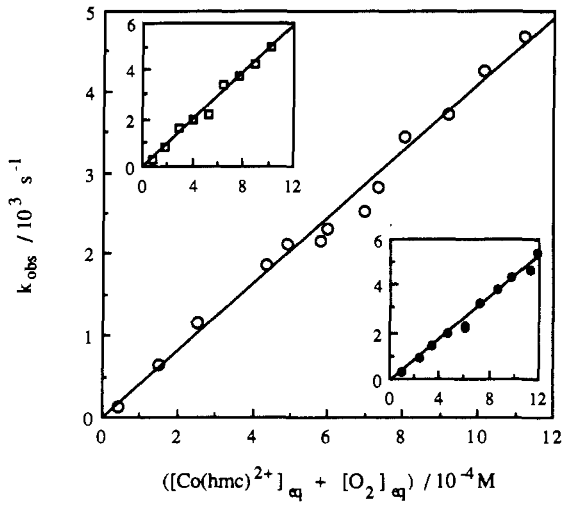

Figure 1. Plot according to eq 4 for the reaction of $Co(hmc)^{2+}$ with O_2 at pH 9.82 (0.05 M im, circles). The respective plots for pH 9.47 (0.5 M py, squares) and 9.82 (0.05 M 1-Meim, dots) are shown in insets.

Table I. Apparent Rate Constants for the Binding and Release of Oxygen by $Co(hmc)^{2+}$ in Aqueous Solutions[a]

pH[b]	$k_f^{app}/10^6$ M^{-1} s^{-1}	$k_h^{app}/10^2$ s^{-1}	medium (concn/mM)
5.0[c]		217 (8)	py (556) + CF_3SO_3H (356)
5.46	4.59 (25)	182 (2)	H_2O
5.48[d]	5.00 (47)	166 (5)	H_2O
6.5	3.54 (121)	97.2 (102)	py (527) + CF_3SO_3H (27)
9.12		2.01 (24)	py (100)
9.47	4.94 (21)		py (500)
9.48		0.409 (44)	im (10)
9.82	4.10 (14)		im (50)
9.82	4.51 (16)		1-Meim (50)
12.0	2.09 (9)		NaOH (10)
13.0	1.08 (16)		NaOH (100)

[a] hmc = *C-meso*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane. All the kinetic data were obtained by laser flash photolysis, except those at pH 9.12 and 9.48, which were acquired by stopped-flow. [b] Calculated from the respective pK_a values and checked by pH-metric measurements. [c] Because of a considerable scatter of data, the k_f value was fixed in the calculations at 5.00 (47) × 10^6 M^{-1} s^{-1}. [d] Reference 11.

complications would arise from the growing excess of the oxygen-free Co(II) complex produced in the course of such an experiment.

A number of prospective scavengers were tested for their usefulness in the kinetic experiments, but only two, $ABTS^{\bullet-}$ and *t*-BuOOH, worked well. $ABTS^{\bullet-}$ was slowly reduced by imidazole and somewhat faster by SCN^-, but these side reactions did not interfere with the much faster loss of $ABTS^{\bullet-}$ in the reactions of interest. The 1:1 stoichiometry of the reaction of $ABTS^{\bullet-}$ with $Co(hmc)^{2+}$ was determined by a spectrophotometric titration.

The second-order rate constant for the reaction of $Co(hmc)^{2+}$ with $ABTS^{\bullet-}$ was found not to be affected by the presence of pyridine or imidazole in concentrations used in the scavenging experiments. This was another indication that these bases do not form complexes with $Co(hmc)^{2+}$. Averaged data yielded k_{Sv} = (7.10 ± 0.24) × 10^5 M^{-1} s^{-1}.

This value is much too small to make $k_{Sv}[Sv] \gg k_f^{app}[O_2]$, i.e. to reduce eq 7 to $k_{obs} = k_h^{app}$. In a typical experiment the concentration of free O_2 is 1.27 mM, and the maximum concentration of $ABTS^{\bullet-}$ is ~0.1 mM. Thus a k_{Sv} of $\geq 6.4 \times 10^9$ M^{-1} s^{-1} would be required to make $k_{obs} = k_h^{app}$. In fact, the situation is entirely reversed and $k_f^{app}[O_2] \gg k_{Sv}[Sv]$, which reduces eq 7 to its other extreme, $k_{obs} = k_h^{app}k_{Sv}[Sv]/(k_f^{app}[O_2])$. A plot of k_{obs} against $[Sv]/[O_2]$, shown in Figure 2, yielded values of $k_h^{app}k_{Sv}/k_f^{app}$. By substitution of the previously determined k_f^{app} and k_{Sv} values, the rate constants for homolysis of the Co–O_2 adduct were calculated to be 201 ± 24 s^{-1} (0.1 M py, pH 9.12) and 40.9 ± 4.4 s^{-1} (0.01 M im, pH 9.48).

Kinetics of Homolysis of Co(hmc)(SCN)O_2^+. The kinetics of the reaction of $Co(hmc)(NCS)^+$ with $ABTS^{\bullet-}$ were determined by laser flash photolysis using $Co(hmc)(CH_3)^{2+}$ as a photochemical precursor to $Co(hmc)^{2+}$, eq 8.[11] In the presence of O_2,

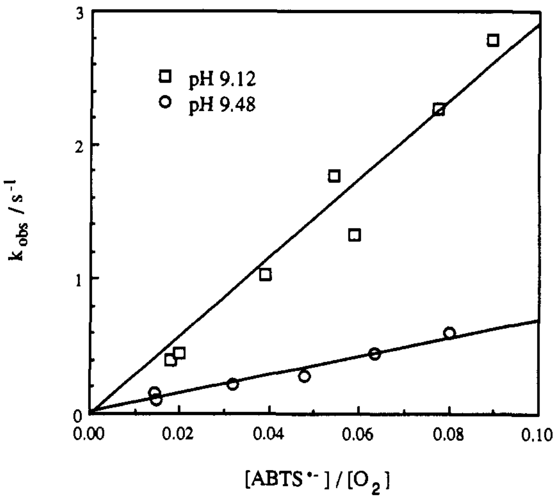

Figure 2. Plots according to eq 7 ($k_{Sv}[Sv] \ll k_f[O_2]$) for the homolysis of the Co–O_2 adduct in the presence of $ABTS^{\bullet-}$ as scavenger. Data are shown for pH 9.12 (0.1 M py, squares) and 9.48 (0.01 M im, circles).

$$Co(hmc)(CH_3)^{2+} \xrightarrow{h\nu} Co(hmc)^{2+} + {}^{\bullet}CH_3 \qquad (8)$$

SCN^-, and $ABTS^{\bullet-}$ in the photolyzed solutions reactions 9–13 take place.[24]

$$^{\bullet}CH_3 + O_2 \rightarrow CH_3O_2^{\bullet} \qquad (9)$$

$$^{\bullet}CH_3 + ABTS^{\bullet-} \rightarrow \text{adduct} \qquad (10)$$

$$Co(hmc)^{2+} + NCS^- \rightleftarrows Co(hmc)(NCS)^+ \qquad (11)$$

$$Co(hmc)(NCS)^+ + O_2 \rightleftarrows Co(hmc)(NCS)O_2^+ \quad k_f, k_h \qquad (12)$$

$$Co(hmc)(NCS)^+ + ABTS^{\bullet-} \xrightarrow{k_{Sv,13}} Co(hmc)(NCS)^{2+} + ABTS^{2-} \qquad (13)$$

At the high $[SCN^-]$ used (0.1 M) the equilibrium in eq 11 lies completely to the right.[12] With the use of known rate constants for eqs 9, 10, and 12 and the stopped-flow estimate for $k_{Sv,13}$, it was possible to calculate for an air-saturated solution a range of $[ABTS^{\bullet-}]$ for which practically all methyl radicals react with oxygen and simultaneously most of the cobalt(II) is oxidized by $ABTS^{\bullet-}$. In that case the rate law of eq 14 applies (Figure 3, Sv

$$k_{obs} = k_f[O_2] + k_{Sv,13}[Sv] \qquad (14)$$

= $ABTS^{\bullet-}$). With k_f fixed at its known value (7.29 × 10^6 M^{-1} s^{-1}),[12] the data in Figure 3 yielded $k_{Sv,13}$ = (2.93 ± 0.03) × 10^8 M^{-1} s^{-1}.

The combination of this value and the concentration requirements in the determination of k_h made it impossible for eq 7 to be used in either of its limiting forms. The data were fitted to the full form of eq 7, with $k_{Sv,13}$ and k_f fixed at their experimental values. The fit yielded k_h = 17.7 ± 0.3 s^{-1}. Even when both $k_{Sv,13}$ and k_f were allowed to float, the values obtained for each were within 3% of those given above. This strongly supports the reaction scheme proposed.

tert-Butyl hydroperoxide was also used as a scavenger for Co(II). Unfortunately, it oxidizes Co(II) slowly, and only in the

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(24) Other possible reactions that could involve Co(II) were discussed in ref 11 and concluded to be negligible. Also, no other products seem to be able to react with $ABTS^{\bullet-}$ to a measurable extent.

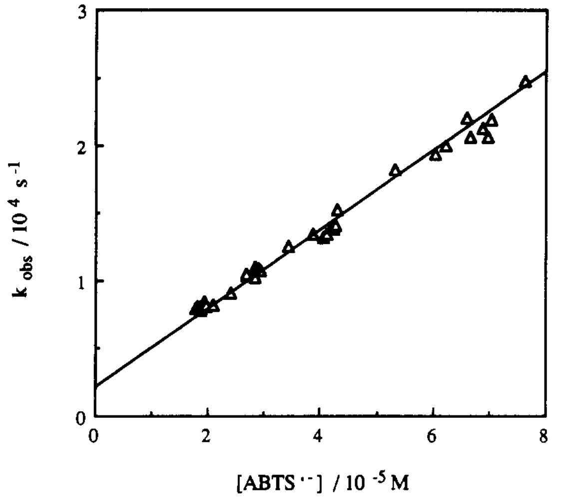


Figure 3. Plot according to eq 14 (with k_f value fixed) for the reaction of $Co(hmc)(SCN)^+$ with $ABTS^{•-}$ and O_2.

Table II. Second-Order Rate Constants for the Reactions of $Co^{II}(hmc)L^{n+}$ Complexes with Scavengers

complex	scavenger	$k_{Sv}/M^{-1}\,s^{-1}$
$Co(hmc)^{2+}$	$ABTS^{•-}$	$7.10\ (24) \times 10^5$
$Co(hmc)(SCN)^+$	$ABTS^{•-}$	$2.93\ (3) \times 10^8$
$Co(hmc)(SCN)^+$	*t*-BuOOH	$5.30\ (26) \times 10^1$

presence of thiocyanate ion was *t*-BuOOH suitable for scavenging experiments. The kinetics of the reaction of $Co(hmc)(SCN)^+$ with excess *t*-BuOOH was monitored at an absorption maximum of the complex at 490 nm. As a result, $k_{Sv,ROOH} = 53.0 \pm 2.6$ $M^{-1}\,s^{-1}$ was obtained. All the values of k_{Sv} are collected in Table II. Spectrophotometric titrations yielded a ratio [*t*-BuOOH]/[$Co(hmc)(SCN)^+$] = 1.00 ± 0.05.

For such a low value of $k_{Sv,ROOH}$ the second term in the denominator of eq 7 was negligible again. Accordingly, the observed rate constant for the decay of the $Co(hmc)(SCN)O_2^+$ absorbance at 465 nm in the presence of excess *t*-BuOOH was proportional to the concentration of *t*-BuOOH. From a plot analogous to that in Figure 2 a value of $k_h = 35.9 \pm 3.6\ s^{-1}$ was derived. This treatment assumes that the stoichiometry of the cobalt(II)–*tert*-butyl hydroperoxide reaction remains 1:1 in the presence of O_2. Note that this value of k_h is twice as large as that obtained with $ABTS^{•-}$, as discussed later.

Role of Equilibria in the Formation of $Co(hmc)LO_2^{n+}$. The acidity constants of both $Co(hmc)(H_2O)_2^{2+}$ and $Co(hmc)(H_2O)O_2^{2+}$ were determined by injecting a small volume of stock $Co(hmc)^{2+}$ into O_2-free or O_2-saturated aqueous solutions buffered at the desired pH, followed by absorbance measurements at 500 nm and 320 nm, respectively. The absorbances were recorded for 1–2 min and extrapolated to the moment of injection. Carbonate and phosphate buffers and sodium hydroxide solutions were used to study the deprotonation of $Co(hmc)(H_2O)_2^{2+}$, whereas mixtures of pyridine and trifluoromethanesulfonic acid were used in the case of $Co(hmc)(H_2O)O_2^{2+}$. All the results were self-consistent, and the nature of the buffer had no effect on the outcome of these measurements. The data are shown in Figure 4, and the values obtained are $pK_a = 11.68 \pm 0.04$, $\Delta\epsilon_{500} = 30 \pm 1\ M^{-1}\,cm^{-1}$ for $Co(hmc)(H_2O)_2^{2+}$ and $pK_a = 6.42 \pm 0.02$, $\Delta\epsilon_{320} = 4200 \pm 300\ M^{-1}\,cm^{-1}$ for $Co(hmc)(H_2O)O_2^{2+}$.[25]

The dependencies of k_f^{app} and k_h^{app} on pH can be rationalized once the protonation equilibria of the substrates are included into kinetic equations. Provided that a single acid/base equilibrium exists for the reactants, and another one for the products, then the following relation applies to both forward and reverse reactions:

$$k^{app} = \frac{k^{H_2O} + k^{OH}\,10^{(pH-pK_a)}}{10^{(pH-pK_a)} + 1} \tag{15}$$

Here k^{H_2O} and k^{OH} denote the rate constants for the reactions of acidic and basic forms, respectively. The data in Table I were fitted to eq 15 by nonlinear least-squares methods at fixed pK_a values (Figure 5). Since k_h^{OH} is several orders of magnitude lower than $k_h^{H_2O}$, the fitting did not yield a reasonable value for the former rate constant, which was then fixed at 0. With that, the remaining three rate constants are as follows: $k_f^{OH} = (8.9 \pm 2.7) \times 10^5\ M^{-1}\,s^{-1}$ for O_2 binding to $Co(hmc)(OH)(H_2O)^+$, $k_f^{H_2O} = (4.65 \pm 0.14) \times 10^6\ M^{-1}\,s^{-1}$ for O_2 binding to $Co(hmc)(H_2O)_2^{2+}$, and $k_h^{H_2O} = (2.06 \pm 0.07) \times 10^4\ s^{-1}$ for O_2 release from $Co(hmc)(H_2O)O_2^{2+}$. The latter two are close to those found previously below pH 7.[11]

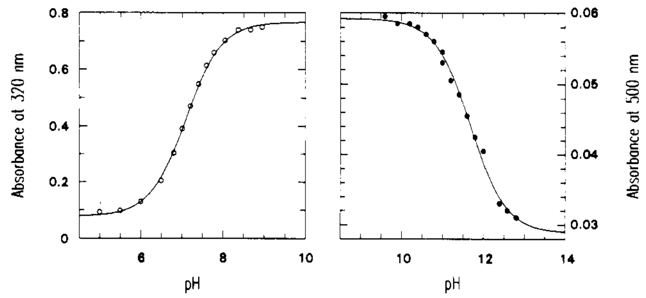


Figure 4. Plots of absorbance (1 cm cells) vs pH for $Co(hmc)(H_2O)O_2^{2+}$ (left, total [Co] = 0.1 mM) and $Co(hmc)(H_2O)_2^{2+}$ (right, total [Co] = 1 mM).

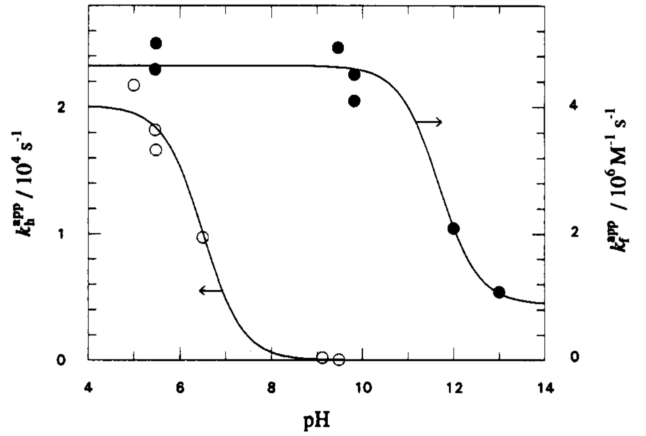


Figure 5. Dependence of k_f^{app} (dots) and k_h^{app} (circles) on pH. Data from Table I were fitted to eq 15 with pK_a values fixed at their known values.

The instability of the strongly alkaline solutions of the complexes prevented us from acquiring the k_f^{OH} with better accuracy and made it impossible to measure directly the slow rate of oxygen release from $Co(hmc)(OH)O_2^+$. Attempts to calculate k_h^{OH} from eq 15 by using k_h^{app} measured in py and im indicated that it cannot be clearly distinguished from the contribution to k_h^{app} from a small equilibrium concentration of the much more reactive protonated form of the complex. Similar calculations for homolysis of $Co(hmc)(SCN)O_2^+$ showed that the contribution from $Co(hmc)(H_2O)O_2^{2+}$ is 0.87 s^{-1}, a little more than the standard deviation of k_h^{SCN}.

There remains still another way to calculate k_h^{OH}. If the deprotonation of the aqua ligand is treated as coordination of OH^-, then Scheme I and eq 16 can be used ($K_{OH} = K_a \times 10^{14}$ M^{-2}) to calculate $K_{O_2}^{CoOH} = (4.18 \pm 0.87) \times 10^7\ M^{-1}$. The formation rate constant for $Co(hmc)(OH)O_2^+$, $k_f^{OH} = (8.9 \pm 2.7) \times 10^5\ M^{-1}\,s^{-1}$, divided by $K_{O_2}^{CoOH}$ yields the homolysis rate constant $k_h^{OH} = 0.021 \pm 0.011\ s^{-1}$. The summary of all the kinetic and equilibrium data is given in Table III.

$$K_{OH}^{Co}\,K_{O_2}^{CoOH} = K_{O2}^{Co}\,K_{OH}^{CoO_2} \tag{16}$$

Discussion

The lack of coordination of pyridine, imidazole, and 1-methylimidazole to $Co(hmc)^{2+}$ was surprising, since their role in the

Scheme I

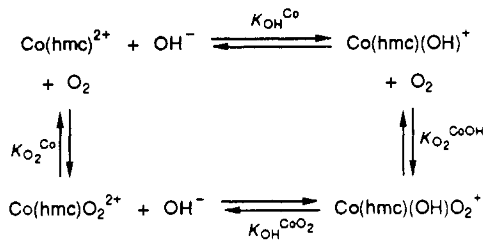
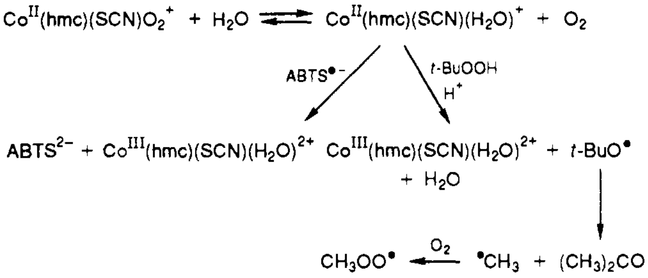


Table III. Summary of the Kinetic and Equilibrium Data for the Formation and Homolysis of $Co(hmc)LO_2^{n+}$ [a] in Aqueous Solutions at 25 °C

L	$k_f/10^6$ M^{-1} s^{-1}	k_h/s^{-1}	$K_{O_2}^{CoL}/M^{-1}$ [b]	K_L^{Co}/M^{-1}
H_2O[c]	5.00 (47)	1.66 (5) × 10^4	3.01 (40) × 10^2	(1)
H_2O	4.65 (14)	2.06 (7) × 10^4	2.31 (16) × 10^2	(1)
Cl^- [d]	1.80 (26)	3.21 (20) × 10^3	5.6 (12) × 10^2	3.8
SCN^-	7.29 (14)[d]	1.77 (3) × 10^1 [e]	4.12 (16) × 10^5	174[d]
OH^-	0.89 (27)	2.1 (11) × 10^{-2} [f]	4.18 (87) × 10^7 [g]	209

[a] n = 1 or 2; hmc = *C-meso*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane. [b] Calculated as $K_{O_2}^{CoL} = k_f/k_h$, except for L = OH^-. [c] Reference 11. [d] Reference 12. [e] With $ABTS^{\bullet-}$ as scavenger for Co(II). [f] Calculated from k_f and $K_{O_2}^{CoL}$. [g] Determined experimentally ($=K_{O_2}^{CoOH}$; see text).

Scheme II



formation of other Co–O_2 adducts is well documented in the literature,[1,2] including a recent report on a Co–N_4 macrocycle in aqueous solution.[26] A proper recognition of the role of the Lewis bases in the course of the present study was made additionally difficult because the equilibrium constants for the base coordination were expected to be small.[26] However, a careful investigation over a wide pH range revealed that the apparent effect of py, im, and 1-Meim on the kinetics and thermodynamics of oxygen binding and release can be accounted for by the acid/base equilibria of $Co(hmc)(H_2O)_2^{2+}$ and $Co(hmc)(H_2O)O_2^{2+}$. The axial ligand that influences the homolysis of the cobalt-oxygen bond in these systems is actually the hydroxide ion.

A remarkable difference in K_a between the dioxygen and oxygen-free complexes (>5 orders of magnitude) implies a high degree of electron transfer from Co to O_2 in $Co(hmc)(H_2O)O_2^{2+}$.

Coordinated axial bases greatly influence the thermodynamics and kinetics of oxygen binding to $Co(hmc)^{2+}$. Indeed, there is a qualitative correlation between the equilibrium constants for the binding of a given base to cobalt(II) and that for the binding of the resulting $Co(hmc)L^{n+}$ to oxygen, as shown in Table III. Perhaps this is not surprising: the base that best donates electron density to cobalt is the one that promotes electron transfer to oxygen and thus stabilizes the oxygen adduct toward homolysis.

This thermodynamic argument is, however, not reflected in the kinetics of the oxygen binding step. Here, the range of rate constants is quite small, (0.9 – 7.3) × 10^6 M^{-1} s^{-1}. This can be rationalized by invoking ligand substitution and intramolecular electron transfer as separate steps.

$$Co^{II}(hmc)L(H_2O)^{n+} + O_2 \rightleftarrows \{Co^{II}(hmc)L(O_2)\}^{n+} + H_2O \tag{17}$$

$$\{Co^{II}(hmc)L(O_2)\}^{n+} \rightleftarrows \{Co^{III}(hmc)L(O_2^-)\}^{n+} \tag{18}$$

In a general case this scheme gives

$$k_f = \frac{k_{17}}{1 + (k_{-17}/k_{18})} \text{ and } k_h = \frac{k_{-18}}{1 + (k_{18}/k_{-17})} \tag{19}$$

We suggest that the invariance of k_f with the identity of the base implies that the system may approach the limiting case $k_f \approx k_{17}$; i.e., electron transfer in the forward direction is fast compared to substitution by an I_D mechanism. Apparently the base influences only the electron-transfer step. Indeed, were the effect of L on the Lewis acidity of the cobalt(II) important, the more strongly bound bases should have reduced the capacity of cobalt to bind oxygen, exactly opposite to what has been observed. In the limit where $k_f \approx k_{17}$, we necessarily have $k_h \approx k_{-18}k_{-17}/k_{18} \approx k_{-17}/K_{18}$. The appearance of the equilibrium constant $1/K_{18}$ in this term causes the wide rate variation found. By itself k_{-17}, like k_{17}, would show little variation with base, or an opposite one. But the better the Lewis base is (larger K_L^{Co}) the larger the value of K_{18} and the smaller therefore the rate constant for homolysis. As yet, a means of measuring the intramolecular rate constant in eq 18 has not been devised.

The two values of k_h for $Co(hmc)(SCN)O_2^+$ were determined by use of $ABTS^{\bullet-}$ (k_h = 18 s^{-1}) and *t*-BuOOH (k_h = 36 s^{-1}) as scavengers for $Co(hmc)(SCN)O_2^+$. Their chemistry is detailed in Scheme II.

Despite the factor of 2 variance, each method by itself seems valid. We suggest that the *t*-BuOOH value is a factor of 2 too high, i.e., that the rate constant measured is really $2k_h$. This would happen if *tert*-butoxy or methylperoxy radicals oxidize a second mole of the cobalt–oxygen complex. The oxidation could be either direct, eq 20, or mediated by $(SCN)_2^{\bullet-}$, eqs 21 and 22.

$$Co(hmc)(SCN)O_2^+ + t\text{-}BuO^\bullet \text{ (or } CH_3OO^\bullet) \rightarrow (H_2O)Co(hmc)(SCN)^{2+} + O_2 + t\text{-}BuOH \text{ (or } CH_3OOH) \tag{20}$$

$$t\text{-}BuO^\bullet \text{ (or } CH_3OO^\bullet) + 2SCN^- \rightarrow (SCN)_2^{\bullet-} + t\text{-}BuOH \text{ (or } CH_3OOH) \tag{21}$$

$$(SCN)_2^{\bullet-} + Co(hmc)(SCN)O_2^+ \rightarrow 2SCN^- + (H_2O)Co(hmc)(SCN)^{2+} + O_2 \tag{22}$$

(Note that SCN^- is present at 0.1 M level.) There is as yet no method of checking this directly, but our preliminary results show that the related superoxochromium ion, $(H_2O)_nCrO_2^{2+}$, can be oxidized by $Ru(bpy)_3^{3+}$ to yield Cr^{3+} and O_2. Equations 20 and 22 were written in analogy with this reaction.

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(25) The latter case was somewhat complicated in that the aqua form exists in equilibrium defined by $K_{O_2}^{Co}$ with the oxygen-free complex. Thus, the pH–absorbance data were fitted to the equation

$$A_{320} = [Co]_T \frac{f\epsilon_f + \epsilon_p + \epsilon_d 10^{(pH-pK_a)}}{10^{(pH-pK_a)} + f + 1}$$

where $f = 1/(K_{O_2}^{Co}[O_2]_{av})$, and ϵ_f, ϵ_p, and ϵ_d denote extinction coefficients at 320 nm for $Co(hmc)(H_2O)_2^{2+}$, $Co(hmc)(H_2O)O_2^{2+}$, and Co(hmc)-$(OH)O_2^+$, respectively (the value of ϵ_f = 40 M^{-1} cm^{-1} was fixed in these calculations).

(26) Ye, N.; Busch, D. H. *Inorg. Chem.* **1991**, *30*, 1815.