Molecular Oxygen, Superoxide, and Peroxide as Ligands in a CoN5 Complex[†]

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The cobalt(II) complex $(papd)Co^{II}(H_2O)^{2+}$ (papd = 1,5,8,11,15-pentaazapentadecane) reacts with molecular oxygen to form a μ-peroxo complex in the traditional Wilkins reaction scheme ($k_1 = 1.4 \times 10^7$ M^{-1} s^{-1}, $k_{-1} = 0.65$ s^{-1}, $k_2 = 1.2 \times 10^7$ M^{-1} s^{-1}, $k_{-2} = 2.24 \times 10^{-6}$ s^{-1}). Formation equilibrium constants are 2.2×10^7 M^{-1} and 1.2×10^{20} M^{-2} for the superoxo and peroxo complexes. The absorption spectra of the intermediate mononuclear superoxo complex and the μ-peroxo complex are very similar. Characterization of the $(papd)Co^{II}H_2O)^{2+}$ precursor, $^4T_{1g}(O_h)$, $pK_a((papd)Co(H_2O/OH)^{2+/+}) = 12.6$, $E^\circ((papd)Co(H_2O)^{3+/2+}) = 0.05$ V, allows the calculation of the ligating properties of the superoxide and peroxide ions toward $(papd)Co^{II}(H_2O)^{3+}$, $K((papd)Co^{III}(H_2O)^{3+} + O_2^-) = 10^{12}$ M^{-1} and $K(2(papd)Co^{III}(H_2O)^{3+} + O_2^{2-}) = 2 \times 10^{37}$ M^{-2}.

Introduction

The investigation of the coordinative properties of molecular oxygen, superoxide, and peroxide is of interest from different points of views. This is reflected by an abundance of recent publications on catalysis[1a–c] and electrochemistry,[1c–d] on the relevant bio-inorganic chemistry of copper,[1e–h] iron,[1i–l] and other metals,[1m–o] and on theoretical investigations.[1p–q]

Formally, the formation of a metal–dioxygen complex can be written in a range of ways. The metal ion of the appropriate charge ($x+$) can react either with molecular oxygen, superoxide, or peroxide (O_2^{y-}) to give the $M(O_2)^{x-y}$ product (other ligands on M are omitted):

$$M^{x+} + O_2^{y-} \rightleftharpoons M-O_2^{x-y} \tag{1}$$
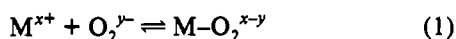
The oxidation states of the metal center and the dioxygen unit in the $M-O_2^{x-y}$ product are defined by its ground-state electron distribution. They are independent of the oxidation states of the starting materials. The extreme noninnocence of the dioxygen unit in conjunction with the range of accessible oxidation states of transition metals precludes an a priori definition of the charge distribution in the dioxygen complex.[2] Equilibrium constants for the above reaction are straightforwardly defined for any pair of corresponding oxidation states of the starting materials

independent of the electron distribution in the product (e.g. $M^{4+} + O_2^{2-} \rightleftharpoons M-O_2^{2+}$, $M^{3+} + O_2^{-} \rightleftharpoons M-O_2^{2+}$, or $M^{2+} + O_2 \rightleftharpoons M-O_2^{2+}$). However, even if all these formation constants are formally correct, only the one is straightforwardly interpretable for which the oxidation states of the educts match the electronic structure of the product.

Among the best investigated dioxygen complexes are the reaction products of molecular oxygen with a wide variety of Co(II) complexes. A series of reviews has been published.[3] Most commonly the products formed have a binuclear μ-peroxo-dicobalt(III) structure. The charge distribution in these binuclear products is apparently well defined. Evidence for the peroxo state of the dioxygen bridge is gained from X-ray structure determinations as well as from IR and Raman investigations. O–O distance and O–O stretching frequencies are significantly different for the possible oxidation states of the dioxygen moiety, and therefore a unique characterisation is possible.[3a–d,4] With pentadentate ligands or ligand systems, mono-bridged μ-peroxo-dicobalt(III) complexes are formed, with tetradentate ligands the products have a doubly bridged μ-peroxo–μ-hydroxo–dicobalt(III) structure. We will concentrate in this contribution on the singly bridged μ-peroxo complexes. Fewer mononuclear dioxygen complexes of cobalt have been synthesized and characterized in aqueous solutions.[5] X-ray, IR, and ESR investigations strongly indicate a superoxo–Co(III) structure.[3a,b,d,6]

Many potentiometric equilibrium studies have been published on the oxygenation of Co(II) complexes[3d] in aqueous solution. They are based on the reaction

$$2LCo(H_2O)^{2+} + O_2 \rightleftharpoons LCo-O_2-CoL^{4+} \tag{2}$$

where L is a pentadentate ligand or ligand system. Equilibrium 2 is defined as the reaction of molecular oxygen with two Co(II) complexes. Because of the change in the oxidation states of both the metal centers and the dioxygen unit upon formation of the binuclear product, the equilibrium constant for eq 2 is formally

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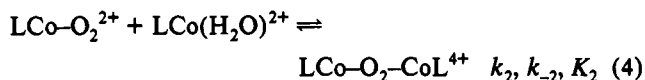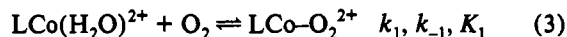 ® Abstract published in *Advance ACS Abstracts*, May 15, 1994.
 (1) (a) Sobkowiak, A.; Sawyer, D. T. *J. Am. Chem. Soc.* **1991**, *113*, 9520–9523. (b) Scott, S. L.; Bakac, A.; Espensen, J. H. *Inorg. Chem.* **1991**, *30*, 4112–4117. (c) Shi, C.; Anson, F. C. *J. Am. Chem. Soc.* **1991**, *113*, 9564–9570. (d) Sazou, D.; Araullo-McAdams, C.; Han, B. C.; Franzen, M. M.; Kadish, K. M. *J. Am. Chem. Soc.* **1990**, *112*, 7879–7886. (e) Sanyal, I.; Strange, R. W.; Blackburn, N. J.; Karlin, K. D. *J. Am. Chem. Soc.* **1991**, *113*, 4692–4693. (f) Karlin, K. D.; Wei, N.; Jung, B.; Kaderli, S.; Zuberbühler, A. D. *J. Am. Chem. Soc.* **1991**, *113*, 5868–5870. (g) Kitajima, N.; Koda, T.; Iwata, Y.; Moro-oka, Y. *J. Am. Chem. Soc.* **1990**, *112*, 8833–8839. (h) Kitajima, N.; Koda, T.; Hashimoto, S.; Kitagawa, T.; Moro-oka, Y. *J. Am. Chem. Soc.* **1991**, *113*, 5664–5671. (i) Traylor, T. G.; Xu, F. *J. Am. Chem. Soc.* **1990**, *112*, 178–186. (j) Sheu, C.; Sobkowiak, A.; Jeon, S.; Sawyer, D. T. *J. Am. Chem. Soc.* **1990**, *112*, 879–881. (k) Menage, S.; Brennan, B. A.; Juarez-Garcia, C.; Münck, E.; Que, L., Jr. *J. Am. Chem. Soc.* **1990**, *112*, 6423–6425. (l) Yamazaki, I.; Piette, L. H. *J. Am. Chem. Soc.* **1991**, *113*, 7588–7593. (m) Bossek, U.; Wyermüller, T.; Wieghardt, K.; Nuber, B.; Weiss, J. *J. Am. Chem. Soc.* **1990**, *112*, 6387–6388. (n) Vaarstra, B. A.; Xiao, J.; Cowie, M. *J. Am. Chem. Soc.* **1990**, *112*, 9425–9426. (o) Barbaro, P.; Bianchini, C.; Mealli, C.; Meli, A. *J. Am. Chem. Soc.* **1991**, *113*, 3181–3183. (p) Lin, W.-K.; Alcock, N. W.; Busch, D. H. *J. Am. Chem. Soc.* **1991**, *113*, 7603–7608. (q) Maddaluno, J.; Giessner-Pretre, C. *Inorg. Chem.* **1991**, *30*, 3439–3445.
 (2) Taube, H. *Prog. Inorg. Chem.* **1986**, *34*, 607–625.

 (3) (a) Valentine, J. S. *Chem. Rev.* **1973**, *73*, 235–245. (b) Gubelmann, M. H.; Williams, A. F. *Struct. Bonding* **1983**, *55*, 1–65. (c) Fallab, S.; Mitchell, P. R. *Adv. Inorg. Bioinorg. Mech.* **1984**, *3*, 311–377. (d) Niederhoffer, E. C.; Timmons, J. H.; Martell, A. E. *Chem. Rev.* **1984**, *84*, 137–203. (e) Mäcke, H. R.; Williams, A. F. In *Photoinduced Electron Transfer*; Fox, M. A., Chanon, M., Eds.; Elsevier: Amsterdam, 1988; Part D, pp 28–45.
 (4) Nakamoto, K. *Coord. Chem. Rev.* **1990**, *100*, 363–402.
 (5) (a) Shinohara, N.; Ishii, K.; Hirose, M. *J. Chem. Soc., Chem. Commun.* **1990**, 700–701. (b) Marchaj, A.; Bakac, A.; Espenson, J. H. *Inorg. Chem.* **1992**, *31*, 4164–4168.
 (6) Proniewicz, L. M.; Bruha, A.; Nakamoto, K.; Uemori, Y.; Kyuno, E.; Kincaid, J. R. *J. Am. Chem. Soc.* **1991**, *113*, 9100–9104.

a composition of the equilibrium $2LCo(H_2O)^{2+} + O_2 \rightleftharpoons LCo^{II}-O_2-Co^{II}L^{4+}$ and the subsequent stabilization gained by the intramolecular redox process to the $LCo^{III}-O_2{}^{2-}-Co^{III}L^{4+}$ complex.[5b] It is not possible to quantify those two processes individually.

The mechanism of the formation of the μ-peroxo–dicobalt-(III) complexes has been determined as[7]

$$LCo(H_2O)^{2+} + O_2 \rightleftharpoons LCo-O_2{}^{2+} \quad k_1, k_{-1}, K_1 \qquad (3)$$

$$LCo-O_2{}^{2+} + LCo(H_2O)^{2+} \rightleftharpoons$$
$$LCo-O_2-CoL^{4+} \quad k_2, k_{-2}, K_2 \qquad (4)$$

The very high reactivity of the intermediate mononuclear dioxygen complex prevented its direct detection in aqueous solution as no substantial concentration could be reached. In fact, a steady-state approach for $[LCo-O_2{}^{2+}]$ has been used to determine k_1 and the ratio k_2/k_{-1} only.

The complete determination of the reaction scheme (eqs 3 and 4) allows a kinetic definition of the individual equilibrium constants K_1 and K_2, which, however, still suffer from the discrepancy between the oxidation states in starting materials and products. Incorporation of the redox potentials for the $LCo(H_2O)^{3+/2+}$ couple and for the $O_2/O_2{}^-$ and $O_2/O_2{}^{2-}$ couples allows the indirect quantification of the equilibria 5 and 6 in which the oxidation states on both sides of the equilibrium match.

$$LCo(H_2O)^{3+} + O_2{}^- \rightleftharpoons LCo-O_2{}^{2+} \quad K_3 \qquad (5)$$

$$2LCo(H_2O)^{3+} + O_2{}^{2-} \rightleftharpoons LCo-O_2-CoL^{4+} \quad K_4 \qquad (6)$$

All four individual rate constants k_1, k_{-1}, k_2, and k_{-2} have been estimated for L = [14]aneN$_4$ (cyclam)[8,9] and L = [15]aneN$_4$[8] and k_1 and k_{-1} for the sterically hindered Me$_6$[14]aneN$_4$ (hexamethylcyclam)[9] which does not form the binuclear μ-peroxo–dicobalt(III) complex in aqueous solution. There is some controversy about k_1 for L = [14]aneN$_4$[8,9] indicating difficulties in the accurate determination of k_1 by the traditional steady-state approach. It should be noted that the square planar geometry of the tetradentate cyclam unit prevents the formation of an additional hydroxo bridge.

In this contribution we present the reactivity of the complex (papd)Co(II)(H$_2$O)$^{2+}$ (papd = 1,5,8,11,15-pentaazapentadecane) toward molecular oxygen. We also present the characterization of the (papd)Co(H$_2$O)$^{2+}$ precursor, the intermediate superoxo, and final μ-peroxo complex. Papd is a flexible pentadentate N$_5$ ligand which forms five- and six-membered chelate rings. Its strong σ-donor properties are unhindered by steric strain.[10] In fact (papd)Co(H$_2$O)$^{2+}$ exhibits many favourable properties which turned out to be valuable for this detailed kinetic investigation. (a) (papd)Co(H$_2$O)$^{2+}$ has one accessible coordination site and thus forms mono-bridged μ-peroxo complexes only. (b) X-ray structure determination of the μ-peroxo complex showed a δ-configuration,[11] and in no experiments have complications due to conformation equilibria been observed. (c) The flexibility of the ligand allows a strain-free strong complexation of both Co(II) and Co(III). This fact explains the low redox potential of the $LCo(H_2O)^{3+/2+}$ couple and a weak coordination of the water molecule in $LCo(H_2O)^{2+}$ as indicated by the high pK value for its deprotonation. Both these properties turned out to be crucial for the new kinetic approach used in this investigation.

The detailed kinetic investigation was initiated by interesting observations measuring the O$_2$ uptake of (papd)Co(H$_2$O)$^{2+}$ with

the Clark electrode.[12] Under initial conditions of [O$_2$] > [(papd)-Co(H$_2$O)$^{2+}$], the free [O$_2$] reaches immediately a transient minimum which corresponds to an oxygen uptake of about 60% per cobalt complex which is subsequently followed by the release of the excess molecular oxygen to the stoichiometric value of 50%. Similar qualitative observations were made for another L$_5$ ligand system[3c] and more recently for L = cyclam.[5a] Under high [O$_2$] the equilibrium (eqs 3 and 4) is shifted toward $LCo-O_2{}^{2+}$ [5a] and substantial concentrations for the superoxo complex can be achieved. Unfortunately the response of the Clark electrode is too slow for quantitative determination of the kinetics. Therefore a detailed kinetic analysis was performed spectrophotometrically using the stopped-flow technique.

Working with initial concentrations [O$_2$] > [(papd)Co-(H$_2$O)$^{2+}$], an intermediate buildup of the reactive superoxo complex is observed. This is in sharp contrast to the classical steady-state approach for the concentration of the intermediate superoxo complex which demands initial concentrations [O$_2$] $\ll$ [(papd)Co(H$_2$O)$^{2+}$]. This also allows a new approach for the complete determination of the reaction scheme (eqs 3 and 4). With initial concentrations [O$_2$] > [(papd)Co(H$_2$O)$^{2+}$] the two steps in the reaction scheme can be clearly separated: in a first very fast step (papd)Co(H$_2$O)$^{2+}$ reacts, almost completely, to the mononuclear intermediate which allows the determination of k_1. The second step, eq 4, is a second-order reaction which is dramatically slowed down due to the very low concentration of the (papd)Co(H$_2$O)$^{2+}$ reactant after the initial step. Measurement of this second slow step using a diode-array spectrophotometer in conjunction with appropriate software for the analysis of the multivariate data[13] resulted in the absorption spectrum of the intermediate superoxo–Co(III) complex as well as an accurate value for k_2. The relative kinetic stability of the intermediate (papd)Co-O$_2{}^{2+}$ solution further allowed the direct determination of k_{-1} by reaction of (papd)Co-O$_2{}^{2+}$ with edta or H$^+$.

The availability of the pair of absorption spectra for the binuclear μ-peroxo and the mononuclear superoxo complex with otherwise equivalent coordination by the ligand papd is unique. 1:1 adducts have been observed in aqueous solution only for bulky ligands which disfavor the bridging reaction.[5b] This pair of absorption spectra will be discussed in terms of several recent spectroscopic studies on this group of compounds.[14a-e]

The equilibria (eqs 3 and 4) have been determined kinetically. Determination of the standard potential for the (papd)-Co(H$_2$O)$^{3+/2+}$ couple in conjunction with the known potentials for the reduction of molecular oxygen to the superoxide and peroxide allowed the computation of the more relevant constants for the equilibria (eqs 5 and 6). Both equilibrium constants, K_3 and K_4, are significantly higher than other known values.

Experimental Section

Materials. The ligand 1,5,8,11,15-pentaazapentadecane (papd) was synthesized as the pentahydrobromide salt as described.[15] CoCl$_2$·6H$_2$O pa and KCl pa were purchased from Merck. (papd)Co(H$_2$O)$^{2+}$ solutions were prepared by purging acidic solutions of CoCl$_2$ and 1 equiv of the ligand with V^{2+} scrubbed argon for at least 0.5 h. The pH was then adjusted by addition of argon purged concentrated KOH to the desired value. These solutions were stable for hours but showed a high affinity for oxygen.

(7) (a) Simplicio, J.; Wilkins, R. G. *J. Am. Chem. Soc.* **1967**, *89*, 6092–6095. (b) Miller, F.; Wilkins, R. G. *J. Am. Chem. Soc.* **1970**, *92*, 2687–2691.

(8) Wong, C.-L.; Switzer, J. A.; Balakrishnan, K. P.; Endicott, J. F. *J. Am. Chem. Soc.* **1980**, *102*, 5511–5518.

(9) Bakac, A.; Espensen, J. H. *J. Am. Chem. Soc.* **1990**, *112*, 2273–2278.

(10) Hancock, R. D.; Martell, A. E. *Chem. Rev.* **1989**, *89*, 1875–1914.

(11) Zehnder, M.; Thewalt, U. *Z. Anorg. Allg. Chem.* **1980**, *461*, 53–60.

(12) Gnaiger, E.; Forstner, Eds. *Polarographic Oxygen Sensors*; Springer-Verlag: Berlin, 1983.

(13) Maeder, M.; Zuberbühler, A. D. *Anal. Chem.* **1990**, *62*, 2220–2224.

(14) (a) Miskowski, V. M.; Robbins, J. L.; Treitel, I. M.; Gray, H. B. *Inorg. Chem.* **1975**, *14*, 2318–2321. (b) Lever, A. B. P.; Gray, H. B. *Acc. Chem. Res.* **1978**, *11*, 348–355. (c) Miskowski, V. M.; Santarsiero, B. D.; Schaefer, W. P.; Ansok, G. E.; Gray, H. B. *Inorg. Chem.* **1984**, *23*, 172–176. (d) Lever, A. B. P. *Inorganic Electronic Spectroscopy*; Elsevier: Amsterdam, 1984; pp 285–296. (e) Miskowski, V. M. *Comments Inorg. Chem.* **1987**, *6*, 193–207. (f) Tuczek, F.; Solomon, E. I. *Inorg. Chem.* **1992**, *31*, 944–953.

(15) Gampp, H.; Haspra, D.; Maeder, M.; Zuberbühler, A. D. *Inorg. Chem.* **1984**, *23*, 3724–3730.

All solutions were adjusted to an ionic strength of 0.5 using KCl and thermostated at 25 °C.

Kinetic Measurements. A Durrum-Gibson stopped-flow spectrometer fitted with a 2-cm flow cell was used to determine k_1 and k_{-1}. k_2 and k_{-2} were determined on a Hewlett-Packard 8450 diode-array spectrometer. Both instruments were equipped with cell holders thermostated at 25 °C.

k_1 was determined by mixing $(papd)Co(H_2O)^{2+}/(papd)Co(OH)^+$ (depending on pH) of different concentrations with an excess of O_2 in buffered solutions between pH 9.9 and 13.5. Buffers used were 0.01 M borate ($pK = 9.2$) and 2-*tert*-butylaminoethanol ($pK = 11.3$). Typical concentrations were $[O_2] = 1.3 \times 10^{-4}$–$6 \times 10^{-4}$ M and $[(papd)Co-(H_2O)^{2+}] = 4 \times 10^{-5}$–$8 \times 10^{-5}$ M. The measurements were fitted as second-order reactions which gave identical rate constants irrespective of the initial concentrations. Some measurements were performed with a large excess of dioxygen under pseudo-first-order conditions. The kinetics under these conditions is faster, approaching the dead time of the relatively large flow cell. Nevertheless, the measurements resulted in the same second order rate constants.

k_{-1} was determined by reacting $(papd)Co-O_2^{2+}$ with 0.1 M edta of pH 9 or with 0.5 M HCl. First-order reactions were observed in both cases with identical rate constants. Solutions of $(papd)Co-O_2^{2+}$ were prepared by rapidly mixing $(papd)Co(H_2O)^{2+}$ solutions with O_2-saturated solutions by a hand-driven stopped-flow setup. The mixture was injected into one of the drive syringes of the Durrum Gibson stopped-flow spectrometer; the other syringe contained the edta or HCl solution. Kinetic runs for the determination of k_{-1} were done within 5–7 s after the formation of $(papd)CoO_2^{2+}$. Some μ-peroxo complex already formed during this time does not interfere because of its very low reactivity.

k_2. A steady-state approach for $(papd)Co(H_2O)^{2+}$ in the reaction system (eqs 3 and 4) was used and checked by numerical integration of the differential equations. For a typical example of initial concentrations $[O_2] = 8.4 \times 10^{-4}$ M and $[(papd)Co(H_2O)^{2+}] = 9.5 \times 10^{-5}$ M, the calculation showed that 95% of the cobalt(II) complex reacts to $(papd)$-$Co-O_2^{2+}$ and 5% to $(papd)Co-O_2-Co(papd)^{4+}$ within 2 ms. The remaining free $[(papd)Co(H_2O)^{2+}]$ stays below 10^{-8} M confirming the steady-state approach. After the initial stage, $(papd)Co-O_2^{2+}$ reacts formally in a second-order reaction to form the μ-peroxo complex. The rate constant $k_{obs} = k_{-1}k_2/([O_2]k_1)$ was determined by a least-squares fit of the spectral series, using a multivariate fitting program.[13] These calculations deliver also the absorption spectra of the intermediate $(papd)$-$Co-O_2^{2+}$ and the final $(papd)Co-O_2-Co(papd)^{4+}$. The resulting value for k_2 as well as the calculated absorption spectra was independent of initial concentrations. The Hewlett-Packard 8450 diode-array spectrometer was equipped with a hand-driven stopped-flow setup.

k_{-2} was determined spectrophotometrically by decomposing $(papd)$-$Co-O_2-Co(papd)^{4+}$ in 0.1 M edta of pH 9 (eq 4). Measurements between 60 and 31.5 °C were used to extrapolate to 25 °C using the Eyring equation. The first homolytic cleavage $(papd)Co-O_2\cdots Co(papd)^{4+}$ (k_{-2}) is rate determining; the final products are $Co^{II}(edta)$ and molecular oxygen as determined with the Clark electrode. These measurements were performed on the HP diode-array spectrometer.

The reactions (eqs 3 and 4) have been qualitatively confirmed using the O_2-sensitive Clark electrode (Beckman 100801 Fieldlab oxygen analyzer with a Beckman 39550 O_2 electrode assembly). The response of the Clark electrode is too slow for a quantitative kinetic analysis of the fast reactions. Similarly, k_{-2} for the second dissociation reaction (eq 4) could theoretically be determined using the Clark electrode; in this case, however, the reaction is too slow and the long-term stability of the Clark electrode was insufficient for a quantitative analysis. Nevertheless, analyses of the initial slopes of O_2 release are consistent with the spectrophotometric measurements. The overall stoichiometry of formation of $(papd)Co-O_2-Co(papd)^{4+}$ was confirmed by amperometric $[O_2]$ measurements.

Electrochemical Measurements. The redox potentials of the $(papd)$-$Co(OH)^{2+}/(papd)Co(H_2O),(OH)^{2+,+}$ couple were determined by cyclic voltammetry of a 2×10^{-3} M solution of $(papd)Co(OH)^{2+}$ between pH 10.8 and 13.5 on a Metrohm E611 and E612 setup. A three-electrode arrangement with a platinum disk electrode, a platinum wire auxiliary electrode, and saturated calomel reference electrode was used. The scan rate was 10^{-3} V s^{-1}. The series results primarily in the redox potential for the $(papd)Co(OH)^{2+/+}$ couple in conjunction with the protonation of the coordinated hydroxide to $(papd)Co(H_2O)^{2+}$ for the cobalt(II) complex. Incorporation of the deprotonation of the coordinated water in the corresponding $(papd)Co(H_2O)^{3+}$, which was determined spectrophotometrically, allowed the indirect determination for the $(papd)$-$Co(H_2O)^{3+/2+}$ couple.
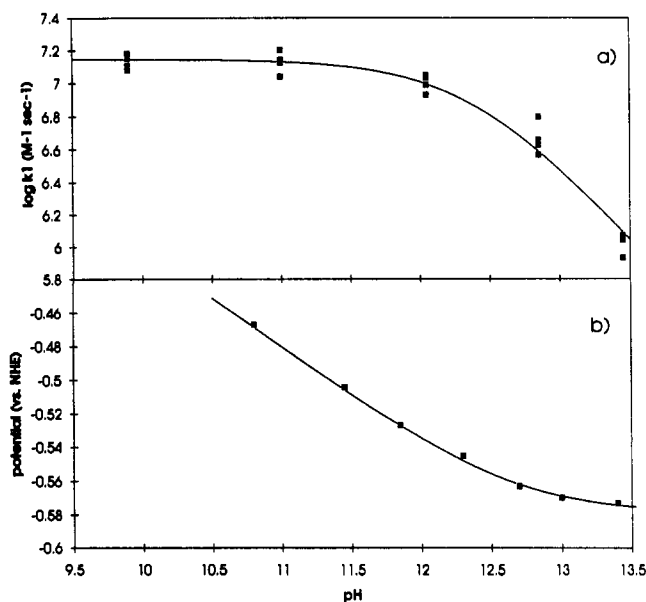
Figure 1. (a) Logarithmic plot of $\log(k_1)$ vs pH. (b) Plot of the redox potential of the $(papd)Co(OH)^{2+}/(papd)Co(H_2O/OH)^{2+/+}$ couple vs pH.

Spin State. The spin state of $(papd)Co(H_2O)^{2+}$ has been determined using the Evans method.[16] A 2×10^{-2} M concentration of $(papd)Co-(H_2O)^{2+}$ (pH 9) in 2% *tert*-butyl alcohol resulted in a shift for the butanol protons of 20 Hz, which transforms to a magnetic moment of $\mu = 4.37$, consistent with a high-spin d^7 electron configuration.

Results

Kinetics. The reactivity of $(papd)Co(H_2O)^{2+}$ toward molecular oxygen has been investigated in aqueous solution at different pH values. The final stable product is a μ-peroxo–dicobalt(III) complex.[11] The particular kinetic properties of $(papd)Co(H_2O)^{2+}$, the intermediate $(papd)Co-O_2^{2+}$, and the product $(papd)Co-O_2-Co(papd)^{4+}$ in conjunction with careful choice of initial concentrations of the starting materials allowed the resolution of the formation reaction into two distinguishable steps (eqs 3 and 4). The formation of $(papd)Co-O_2^{2+}$ and $(papd)Co-O_2-Co-(papd)^{4+}$ (k_1 and k_2) are second-order reactions. The pH dependence of k_1 is shown in Figure 1a. It is straightforwardly interpreted as a deprotonation equilibrium of the coordinated water in $(papd)Co(H_2O)^{2+}$

$$(papd)Co(H_2O)^{2+} \rightleftharpoons (papd)Co(OH)^+ + H^+ \quad pK_a \quad (7)$$
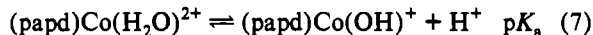
Analysis of the pH dependence yields $k_1 = (1.4 \pm 0.1) \times 10^7$ M^{-1} s^{-1} and a pK_a value for equilibrium (eq 7) of 12.45 ± 0.08. The observed rate constants have been fitted as $k_{obs} = (k_1[H^+])/(K_a + [H^+])$. The hydroxo complex shows no reactivity in the pH region investigated. The contribution of the dissociation reaction ($k_{obs} = k_1[O_2] + k_{-1}$) is negligible.

k_2 has been determined using a steady-state approach for $[(papd)Co(H_2O)^{2+}]$ under initial concentration $[O_2] > [(papd)$-$Co(H_2O)^{2+}]$, $k_2 = (1.2 \pm 0.2) \times 10^7$ M^{-1} s^{-1} at pH < 11. The viability of the steady-state approach after the initial formation of $(papd)Co(O_2)^{2+}$ has been verified by Runge–Kutta calculations.

Characterization of the precursor $(papd)Co(H_2O)^{2+}$ is essential for the understanding of its reactivity toward oxygen in eq 3 and toward $(papd)Co-O_2^{2+}$ in eq 4. It is a high-spin d^7 complex, as determined by the Evans method,[16] with a particularly labile coordinated water molecule. The lability is indicated by the high pK value of 12.6 for its deprotonation which was determined kinetically and electrochemically (see later).

(16) (a) Evans, D. F. *J. Chem. Soc.* **1959**, 2003–2007. (b) Löliger, J.; Scheffold, R. *J. Chem. Educ.* **1972**, *49*, 646–647.

The dissociation reactions in eqs 3 and 4 are first-order reactions. Both have been determined by reacting $(papd)Co-O_2^{2+}$ and $(papd)Co-O_2-Co(papd)^{4+}$ with excess edta. Most probably, the rate-determining step is in both cases the homolytic cleavage of the cobalt–oxygen bond followed by a fast ligand exchange on the kinetically labile $(papd)Co(H_2O)^{2+}$ complex to give Co^{II}-(edta) (charges omitted) which is not reactive toward molecular oxygen.

$$(papd)Co(H_2O)^{2+} + edta \rightarrow Co(edta) + papd \qquad (8)$$
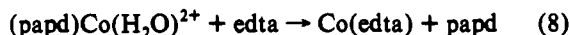
k_{-1} has been determined additionally by decomposition of the superoxo complex in 0.5 M HCl to yield O_2, $papdH_5^{5+}$, and $Co(H_2O)_6^{2+}$. The value for k_{-1} is identical for both reaction, either with edta or with acid, $k_{-1} = 0.65 \pm 0.03\ s^{-1}$. k_{-2} was determined similarly as $k_{-2} = (2.24 \pm 0.05) \times 10^{-6}\ s^{-1}$.

Both dissociation reactions are primarily intramolecular redox processes with the transfer of an electron from either the coordinated superoxide or the μ-peroxide to the Co(III) moiety. The determination of the redox potential of the $(papd)$-$Co(H_2O)^{3+/2+}$ couple was crucial for the understanding of these values.

Redox Potentials. The determination of the standard potential for the $(papd)Co(H_2O)^{3+/2+}$ couple is hampered by deprotonation equilibria of the coordinated water in both oxidation states of the cobalt ion and additionally by the hydrolysis of the $(papd)Co$-$(H_2O)^{2+}$ complex in solutions of pH < 10. The pH dependence of the redox potential as measured by cyclic voltammography gave reversible waves in the pH region investigated; see Figure 1b. The peak separation was about 90 mV at all pH. The interpretation is straightforward: at high pH we observe the $(papd)Co(OH)^{2+/+}$ couple with an extrapolated value of -0.579 ± 0.002 V vs NHE. At lower pH we observe additionally the deprotonation equilibrium of the $(papd)Co(H_2O)^{2+}$ complex. The fitted curve was calculated as $E = E^\circ - 0.06\ \log(K_a/(K_a + H^+))$, and the resulting pK_a value is 12.65 ± 0.07. The corresponding deprotonation equilibrium of $(papd)Co(H_2O)^{3+}$ cannot be determined by cyclic voltammetry because of hydrolysis of $(papd)$-$Co(H_2O)^{2+}$ at the required low pH. This pK_a value has been determined spectrophotometrically to be 6.2. If the deprotonation constants are incorporated, the normal potential of the $(papd)$-$Co(H_2O)^{3+/2+}$ couple is calculated as $+0.05$ V vs NHE.

Absorption Spectra. The absorption spectrum of $(papd)Co$-$O_2-Co(papd)^{4+}$ was determined from solutions of the crystalline dithionate salt.[11] The measurement of the formation kinetics of the μ-peroxo complex with a diode-array spectrometer and subsequent analysis using a multivariate nonlinear least-squares fit yielded the absorption spectrum of $(papd)Co-O_2^{2+}$ and of $(papd)Co-O_2-Co(papd)^{4+}$, which was identical to the one measured from a fresh solution. There is no possibility to determine the spectrum of this highly reactive species directly. Both spectra are shown in Figure 2.

The main feature is the charge-transfer band at 303 nm for the μ-peroxo complex and at 312 nm for the superoxo complex; the molecular absorptivities are 13 000 and 6600 $M^{-1}\ cm^{-1}$, respectively. The superoxo complex shows a distinct absorption band at 436 nm with a molar absorptivity of 400; the μ-peroxo compound exhibits a less defined shoulder in the same region.

Discussion

Kinetics. Both forward reactions are second-order reactions. They can be regarded as multistep processes with an initial ligand exchange followed by an intramolecular electron transfer. In the first reaction the coordinated water molecule in the high-spin $(^4T_{1g}, O_h)$ $(papd)Co(H_2O)^{2+}$ is replaced by O_2, and in the second reaction it is replaced by the $(papd)Co-O_2^{2+}$ ion. The concomitant redox processes are the electron transfers from the $(papd)Co^{II}$ moiety to the molecular oxygen or to the superoxide ligand of the incoming superoxo complex. For several reasons it is safe to
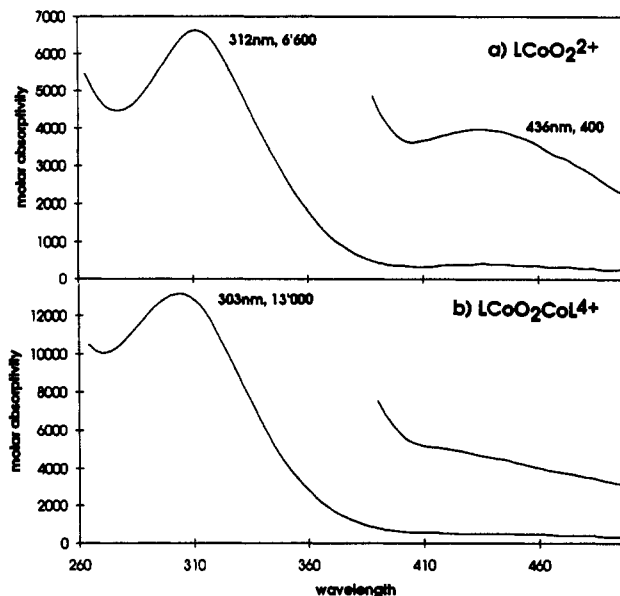
Figure 2. Absorption spectra of (a) $(papd)Co-O_2^{2+}$ and (b) $(papd)$-$Co-O_2-Co(papd)^{4+}$. The insets show the low wavelength part of the spectrum multiplied by a factor of 10.

assume that the water exchange is the rate-determining step and the intramolecular redox process is much faster: (a) the values for k_1 and k_2 are suprisingly similar. The conclusion is further substantiated by the very similar rates for the substitution of the coordinated water in $(cyclam)Co(H_2O)_2^{2+}$ by O_2 ($1.2 \times 10^7\ M^{-1}\ s^{-1}$) and methyl and ethyl radicals (1.6×10^7 and $1.1 \times 10^7\ M^{-1}\ s^{-1}$, respectively).[9] (b) The rate constant k_1 is directly related to the lability of the coordinated water molecule which is reflected by the pK_a value of its deprotonation. For $(papd)Co(H_2O)^{2+}$ k_1 = $1.6 \times 10^7\ M^{-1}\ s^{-1}$ and the deprotonation constant is 12.6; for $(Me_6[14]aneN_4)Co(H_2O)_2^{2+}$, $k_1 = 5 \times 10^6\ M^{-1}\ s^{-1}$ and pK_a = 11.68.[5b] The deprotonation constant has been determined kinetically by measuring the pH dependence of k_1 and electrochemically by measuring the pH dependence of the $(papd)$-$Co^{III/II}(H_2O)$ redox couple. The pK value was determined to be 12.45 as measured kinetically and 12.65 determined electrochemically, a good agreement in view of the relatively cumbersome determinations. (c) The fact that $(papd)Co(OH)^+$ is not reactive toward oxygen is consistent with a rate-determining exchange of H_2O in the oxygenation step. The same retardation of the oxygenation reaction at high pH has been found with the N_5-ligand dptn (1,9-bis(2-pyridyl)-2,5,8-triazanonane) and explained with rate-determining H_2O replacement by O_2.[17] (d) The water exchange rate strongly depends on the ligand field strength of the ligand or ligand system L.[18] (e) It would be surprising to find similar rate constants for the dramatically different reactants O_2 and $O_2-Co(papd)^{2+}$. In fact the corresponding O_2 and O_2-Co-$(cyclam)^{2+}$ couple show very different rates when reacting with reductants in outer-sphere processes.[19] (f) Outer-sphere reaction of O_2 with $Co(sep)^{2+}$ (sep = sepulchrate = 1,3,6,8,10,13,16,19-octaazabicyclo[6.6,6]eicosane) is significantly slower, with a rate constant of 43 $M^{-1}\ s^{-1}$.[20] We exclude an outer-sphere electron transfer as the rate-determining step on the basis of these figures.

The subsequent intramolecular redox processes

$$(papd)Co^{II}-O_2^{2+} \rightarrow (papd)Co^{III}-(O_2^-)^{2+} \qquad (9)$$

(17) Exnar, I.; Mäcke, H. *Helv. Chim. Acta* **1977**, *60*, 2504–2513.
(18) (a) Hunt, J. P. *Inorg. Chem.* **1976**, *15*, 931–933. (b) *Coord. Chem. Rev.* **1971**, *7*, 1–10.
(19) Kumar, K.; Endicott, J. F. *Inorg. Chem.* **1984**, *23*, 2447–2452.
(20) Creaser, I. I.; Geue, R. J.; Harrowfield, J. MacB.; Herlt, A. J.; Sargeson, A. M.; Snow, M. R.; Springborg, J. *J. Am. Chem. Soc.* **1982**, *104*, 6016–6025.

Table 1. Kinetic and Equilibrium Constants for the Oxygenation of Co(II) Complexes

	k_1 (M^{-1} s^{-1})	k_{-1} (s^{-1})	k_2 (M^{-1} s^{-1})	k_{-2} (s^{-1})	K_1 (M^{-1})	K_2 (M^{-1})	K (K_1K_2) (M^{-2})
papd	$(1.4 \pm 0.1) \times 10^7$	0.65 ± 0.03	$(1.2 \pm 0.2) \times 10^7$	$(2.24 \bullet 0.05) \times 10^{-6}$	$(2.2 \pm 0.1) \times 10^7$	$(5.4 \bullet 0.2) \times 10^{12}$	$(1.2 \pm 0.3) \times 10^{20}$
[14]aneN$_4$^{a}	$(5 \pm 1.5) \times 10^5$	63 ± 6	$(4.9 \pm 0.4) \times 10^5$	0.6 ± 0.1	$(8 \pm 2) \times 10^3$	$(8 \pm 3) \times 10^5$	$(6 \pm 3) \times 10^9$
[14]aneN$_4$^{b}	$(1.18 \pm 0.03) \times 10^7$				$2 \times 10^{5\,c}$		$1.6 \times 10^{11\,c}$
[15]aneN$_4$^{a}	$(3.8 \pm 1.1) \times 10^3$	~ 1	$(5 \pm 1) \times 10^4$	~ 2	$\sim 4 \times 10^4$	$\sim 2 \times 10^4$	$10^{8 \pm 1}$
Me$_6$[14]aneN$_4$^{b}	$(5 \pm 0.5) \times 10^6$	$(1.66 \pm 0.05) \times 10^4$			301 ± 40	$<10^3$	

^{a} Reference 8, μ = 0.1–1.0. ^{b} Reference 9, μ = 0.001–0.1. ^{c} Based on k_1 from ref 9 and k_{-1}, k_2, k_{-2} from ref 8.

and

$$(\text{papd})\text{Co}^{\text{II}}\text{-O}_2^-\text{-Co}^{\text{III}}(\text{papd})^{4+} \rightarrow$$
$$(\text{papd})\text{Co}^{\text{III}}\text{-O}_2^{2-}\text{-Co}^{\text{III}}(\text{papd})^{4+} \quad (10)$$

with concomitant electron reconfiguration on the cobalt centers from the high-spin $^4T_{1g}$ (Co(II)) to low-spin $^1A_{1g}$ (Co(III)) are most probably much faster.

The dissociation reactions (k_{-1}, k_{-2}) are first-order reactions. Now, the rate-determining steps in the multistep processes are most probably the intramolecular electron transfers where the electron is transferred either from the coordinated superoxide or the bridging peroxide back to the Co(III) center. Both rates are governed by the normal potentials of the respective reaction partners, i.e. the (papd)Co$^{\text{III/II}}$ couple and either the O$_2$/O$_2^-$ or the O$_2^-$/O$_2^{2-}$ couple and also by the corresponding Franck–Condon factors.[21] To be able to compare the values of the rates of the dissociation reactions for papd with other superoxo and μ-peroxo complexes it is sufficient to concentrate on the redox potentials of the relevant metal centers. The value of +0.05 V for the (papd)Co(H$_2$O)$^{3+/2+}$ couple (N$_5$O) lies between the values for a N$_6$ system (–0.26 V for Co(sep)$^{3+/2+}$)[20] and a N$_4$O$_2$ system (+0.42 V for Co(cyclam)(H$_2$O)$_2$$^{3+/2+}$).[8] Among the complexes with labile oxygen ligands this N$_5$O system exhibits the lowest redox potential, and therefore, the dissociation reactions are the slowest observed values. Refer to Table 1 for a compilation of the published k_{-1} values and to reference[3d] for a compilation of many k_{-2} values for a wide range of ligands.

The equilibrium constants K_1 = 2.2 ± 0.1 × 10^7 M^{-1} for eq 3 and K_2 = 5.4 ± 0.2 × 10^{12} M^{-1} for eq 4 and thus also the total equilibrium (eq 2) K = K_1K_2 = 1.2 ± 0.3 × 10^{20} M^{-2} are the highest observed equilibrium constants.[3d] The main contribution to the high stabilities are the slow dissociation reactions which are governed by the low redox potential of the Co(III)/Co(II) couple. The secondary contribution are the relatively fast forward reactions due to the labile coordinated water.

The combination of those two favorable aspects resulted not only in extreme rate and equilibrium constants; it also allowed the direct and reliable determination of all four rate constants of the formation and dissociation of the mononuclear superoxo and of the μ-peroxo–dicobalt(III) complex. Under appropriate conditions, a transient accumulation of the reactive species (papd)-Co–O$_2$$^{2+}$ is achieved, which in turn allowed the determination of its absorption spectrum. This is in sharp contrast to the traditional approach which works under steady-state low concentrations for the intermediate. Obviously no spectral information can then be obtained about the intermediate superoxo complex.

Absorption Spectra. The absorption spectra of (papd)Co–O$_2$$^{2+}$ and (papd)Co–O$_2$–Co(papd)$^{4+}$ are shown in Figure 2. The main feature in both spectra is the strong band at 312 nm for (papd)Co–O$_2$$^{2+}$ and 303 nm for (papd)Co–O$_2$–Co(papd)$^{4+}$ with molar absorptivities of 13 000 and 6600 M^{-1} cm^{-1}, respectively. Both bands are straightforwardly interpreted as $\pi_s \rightarrow \pi_s^*$ (O$_2^{2-/-} \rightarrow$ Co(III)) ligand to metal charge-transfer processes.[14f] It is interesting to note the twofold increase in molar absorptivity from the mononuclear to the binuclear species. A similar observation has been made for the mono- and binuclear peroxo

and μ-peroxo complex of Cu(II).[22] The superoxide shows a weaker absorption at 436 nm (ϵ 400 M^{-1} cm^{-1}), whereas the μ-peroxide shows an ill-defined shoulder in the same region of the spectrum with a molar absorptivity of about 500 M^{-1} cm^{-1}. This band is due to a convolution of several ligand-field processes in the case of the μ-peroxide[14f] (bands III, IV, V). Most probably the absorption in the superoxide is of the same origin.

Binuclear μ-superoxo–dicobalt(III) complexes exhibit a characteristic d$\pi \rightarrow \pi_s^*$ MLCT around 700 nm.[14a–c] This feature is expected but is not observed in the mononuclear analogue. A reasonable interpretation of the observation would be a shift of the band to lower energy, beyond the 800-nm limit of the spectrometer used.

Secondary Equilibria. The ligands O$_2$, O$_2^-$, and O$_2^{2-}$ play a very important role in biochemistry. The investigation of their ligating properties, however, is seriously hampered by the instability of the superoxide and peroxide ions in the presence of metal ions. This is particularly the case for thermodynamic studies which may require substantial amounts of time for the establishment of the respective equilibria. Nevertheless, kinetic investigations on the reactivity of O$_2^-$ and O$_2^{2-}$ with Co complexes have been published. The reaction of O$_2^{2-}$ with a series of Co(III) hexaamines does not result in substitution reactions but in outer-sphere redox processes with Co(II) and molecular oxygen as primary products.[23] Molecular oxygen as well as the superoxide ion react in outer-sphere reactions with the cage compound Co(sep)$^{2+}$.[20,24]

In this contribution, the equilibrium constants K_3 (eq 5) and K_4 (eq 6) were determined indirectly, combining the kinetically determined equilibrium constants K_1 and K_2 with the potentials for the redox couples (papd)Co(H$_2$O)$^{3+/2+}$ and O$_2^{0/-}$ or O$_2^{0/2-}$. Both equilibria display a rich pH chemistry due to the deprotonation equilibria of (papd)Co(H$_2$O)$^{3+}$, (papd)Co(H$_2$O)$^{2+}$, HO$_2$, and H$_2$O$_2$ in the accessible pH range. Figure 3 displays the pH dependence of the two equilibrium systems

$$(\text{papd})\text{Co(H}_2\text{O/OH)}^{2+/+} + \text{O}_2 + \text{H}^+ \rightleftharpoons (\text{papd})\text{Co-O}_2^{2+} + \text{H}_3\text{O}^+\text{/H}_2\text{O}$$
$$(\text{papd})\text{Co(H}_2\text{O/OH)}^{3+/2+} + \text{HO}_2\text{/O}_2^- + \text{H}^+ \quad (11)$$

$$2(\text{papd})\text{Co(H}_2\text{O/OH)}^{2+/+} + \text{O}_2 + 2\text{H}^+ \rightleftharpoons (\text{papd})\text{Co-O}_2\text{-Co(papd)}^{4+} + 2\text{H}_3\text{O}^+\text{/H}_2\text{O}$$
$$2(\text{papd})\text{Co(H}_2\text{O/OH)}^{3+/2+} + \text{H}_2\text{O}_2\text{/HO}_2 + \text{H}^+ \quad (12)$$

The pK_a values used are pK_a((papd)Co(H$_2$O)$^{2+}$) = 12.6, pK_a-((papd)Co(H$_2$O)$^{3+}$) = 6.2, pK_a(HO$_2$) = 4.7, and pKa(H$_2$O$_2$) = 11.6; the relevant redox potentials are $E°$((papd)Co(H$_2$O)$^{3+/2+}$ = 0.05 V, $E°$(O$_2$/HO$_2$) = 0.12 V, and $E°$(O$_2$/H$_2$O$_2$) = 0.78 V. The values for the couples involving O$_2$ are taken from ref 2; they are based on O$_2$(aq) rather than O$_2$(g) as the standard state for

(21) Marcus, R. A. *J. Chem. Phys.* **1956**, *24*, 966–978.

(22) (a) Pate, J. E.; Cruse, R. W.; Karlin, K. D.; Solomon, E. I. *J. Am. Chem. Soc.* **1987**, *109*, 2624–2630. (b) Baldwin, M. J.; Ross, P. K.; Pate, J. E.; Tyeklar, Z.; Karlin, K. D.; Solomon, E. I. *J. Am. Chem. Soc.* **1991**, *113*, 8671–8679.

(23) McDowell, M. S.; Espenson, J. H.; Bakac, A. *Inorg. Chem.* **1984**, *23*, 2232–2236.

(24) Bakac, A.; Espenson, J. H.; Creaser, I. I.; Sargeson, A. M. *J. Am. Chem. Soc.* **1983**, *105*, 7624–7628.
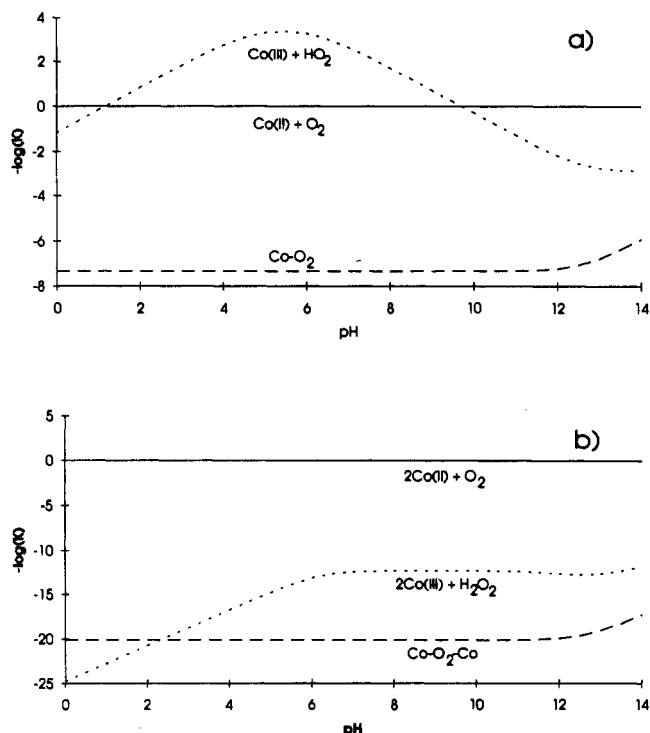
Figure 3. pH dependence of the equilibrium constants for the reaction schemes involving (a) eq 11 and (b) eq 12. The equilibria are represented with respect to (papd)Co^{II} and O$_2$.

O$_2$ and thus are consistent with the definition of the rate constants. The equilibria are defined relatively to (papd)Co^{II} + O$_2$. $-\log$ (K) is plotted to represent the relative energies for the equilibria.

The value for the equilibrium 5 can be read off Figure 3a directly around pH 5 as $K_3 = 10^{12}$ M^{-1}. This extremely high value introduces some doubts about the formulation of the product as an innocent Co(III)–superoxo complex. Structural information, derived from IR and Raman investigations and X-ray structures, on similar mononuclear dioxygen complexes strongly supports this electron distribution. Nevertheless, some resonance stabilization between the two extremes, (papd)Co^{III}–(O$_2^-$)$^{2+}$ and (papd)Co^{II}–(O$_2$)$^{2+}$, is highly probable and is also supported by ESR investigations which indicate some 10% electron density residing on the Co(III) moiety which leads to a 8-line spectrum[5a] due to the hyperfine splitting with the ^{59}Co nucleus ($m = 7/2$) although the interpretation of the ESR spectra is still controversial.[25]

It is interesting to note that (papd)Co^{II} + O$_2$ is stable with respect to (papd)Co^{III} + superoxide only at intermediate pH. However, in the whole accessible pH range the superoxo complex is the thermodynamically stable product.

The equilibrium between 2(papd)Co^{III} + H$_2$O$_2$ and the μ-peroxo complex shows an interesting pH dependence: the complex is unstable toward hydrolysis at pH below 2. Air oxidation of Co(II) complexes is a standard method for the preparation of Co(III) compounds with formation of intermediate μ-peroxo complexes. Surprisingly little is known about the mechanism of the decay of the μ-peroxo complexes to mononuclear Co(III) complexes. Particularly the fate of the peroxide is unknown in most instances.[3c] In line with Figure 3b, H$_2$O$_2$ has been detected only in acidic solution for other ligand systems.[26] Of course secondary reactions can drive the final equilibrium to further products with only intermediate and undetectable formation of H$_2$O$_2$.

According to the diagrams, approaches to synthesize superoxo and μ-peroxo complexes via reaction of Co(III) complexes with O$_2^-$ or O$_2^{2-}$ are theoretically possible. In fact H$_2$O$_2$ has been successfully employed to synthesize μ-peroxo–dicobalt(III) complexes via ligand substitution reactions with aquo–pentamine–Co(III) complexes at high pH.[27]

The hypothetical constant K_4 for eq 6 is calculated as $K_4 = 2 \times 10^{37}$ M^{-2}. A stability per Co–O$_2^{2-}$ bond can be estimated as $\sqrt{K_4} = 4 \times 10^{18}$ M^{-1} which is considerably higher than the value for the Co(III)–superoxo bond. This is in line with the much higher average Brønsted basicity of O$_2^{2-}$ (mean p$K_a \approx 16$) compared to O$_2^-$ (p$K_a = 4.7$).

The photochemistry of binuclear superoxo complexes of Co(III) is well understood.[3a,28] Much less is known about the photochemistry of the μ-peroxo complexes, and recent investigations on the photoactivity of (cyclam)Co–O$_2$–Co(cyclam)$^{4+}$ are somewhat contradictory.[5a,9] Investigations into the photochemistry of (papd)Co–O$_2$–Co(papd)$^{4+}$ show behavior similar to that reported by Shinohara[5a] for the analogous cyclam complex. The photoreaction seems to be

$$(papd)Co-O_2-Co(papd)^{4+} + O_2 \overset{h\nu}{\rightleftharpoons} 2(papd)Co-O_2^{2+} \quad (13)$$
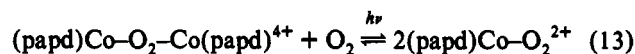
Due to the spectral properties of the two compounds (the product has a similar absorption maximum and half the molar absorptivity of the starting material), the net spectral changes are small.[29] The above equilibrium is dependent on the concentration of the molecular oxygen, and spectral changes are only observable for high [O$_2$]. The knowledge of the pair of absorption spectra of the superoxo and the μ-peroxo complex will allow a thorough analysis of the photochemistry.

(25) Smith, T. D.; Ruzic, I. M.; Tirant, S.; Pilbrow, J. R. *J. Chem. Soc., Dalton Trans.* **1982**, 363–372.

(26) (a) Haim, A.; Wilmarth, W. K. *J. Am. Chem. Soc.* **1961**, *83*, 506–516. (b) Shibahara, T.; Kuroya, H.; Mori, M. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 2834–2838.

(27) (a) Zehnder, M.; Fallab, S. *Helv. Chim. Acta* **1975**, *58*, 13–18. (b) Zehnder, M.; Fallab, S. *Helv. Chim. Acta* **1975**, *58*, 2312–2317.

(28) Valentine, J. S.; Valentine, D. *J. Am. Chem. Soc.* **1971**, *93*, 1111–1117.

(29) Mäcke, H. R.; Maeder, M. Manuscript in preparation.