equatorial–equatorial OC–Co–CO angles of 105° in the two Co(CO)$_3$ groups of [SCo$_3$(CO)$_7$]$_2$S$_2$ and of 101° in SCo$_3$(CO)$_9$; the average equatorial–axial S–Co$_A$–CO angle of 96° is comparable to the identical average equatorial–axial OC–Co$_A$–CO and OC–Co$_B$–CO angles of 100° in [SCo$_3$(CO)$_7$]$_2$S$_2$ and to the corresponding average equatorial–axial OC–Co–CO angle of 101° in SCo$_3$(CO)$_9$.

The salient structural difference between [SCo$_3$(CO)$_7$]$_2$S$_2$ and SCo$_3$(CO)$_9$ is that the average value of 2.64 A for the three equivalent Co–Co bond lengths in SCo$_3$(CO)$_9$ is more than 0.1 A longer than either of the average values of 2.47 and 2.53 A for two sets of Co–Co bonds in [SCo$_3$(CO)$_7$]$_2$S$_2$, whereas the average Co–S$_{ap}$ bond lengths are identical for the two compounds. Clearly, this difference in Co–Co bond lengths must be a consequence of the effect of the disulfide bridge in

[SCo$_3$(CO)$_7$]$_2$S$_2$ and/or the influence of the unpaired electron in SCo$_3$(CO)$_9$. In order to ascertain the relative importance of these two effects, an X-ray study of SFeCo$_2$(CO)$_9$ was carried out; the results of this structural determination will be reported in a future paper.[31]

(31) D. L. Stevenson, C. H. Wei, and L. F. Dahl, to be published.

The Formation of and Interrelation between Some Peroxo Binuclear Cobalt Complexes. I[1]

Masayasu Mori and John A. Weil

Contribution from the Chemistry Division, Argonne National Laboratory, Argonne, Illinois. Received December 6, 1966

Abstract: The interrelations between Werner's green and red μ-amido-μ-peroxo-bis{bis(ethylenediamine)cobalt} salts, [(en)$_2$Co(NH$_2$)(O$_2$)Co(en)$_2$](NO$_3$)$_4$ and [(en)$_2$Co(NH$_2$)(O$_2$)Co(en)$_2$]H(NO$_3$)$_4$·2H$_2$O, respectively, have been reexamined. A brown, diamagnetic complex [(en)$_2$Co(NH$_2$)(O$_2$)Co(en)$_2$](NO$_3$)$_3$·2.5H$_2$O has been obtained from ammoniacal solutions of the green salt, and similarly from the red salt; the brown complex is thought to be the reduced counterpart of the paramagnetic green salt, rather than a complex containing the ion [(en)$_2$Co^{III}(NH)(O$_2$)Co^{IV}(en$_2$)]$^{3+}$, as previously assumed by Werner. The red salt is not simply a protonation product of the brown salt, but rather is a secondary (probably isomeric) product thereof, as is shown by quantitative optical measurements of transformation rates and equilibrium concentrations.

The objective of the present series of studies is to clarify the formation process of and interrelations between various peroxo–dicobalt complexes. The present paper is particularly concerned with the acid–base and oxidation behavior, primarily of Werner's[2a] green and red ethylenediamine series of such compounds.

By the measurement of magnetic susceptibilities, Malatesta[2b] ascertained the presence of one unpaired electron per two cobalt atoms in a series of green μ-peroxo compounds including Werner's green μ-amido-μ-peroxo-bis{bis(ethylenediamine)cobalt} complex. Epr studies by Ebsworth and Weil[3] indicated that such an odd electron is equally distributed with respect to the two cobalt nuclei.

On the other hand, Thompson and Wilmarth[4] studied the red μ-amido-μ-peroxo-bis{bis(ethylenediamine)cobalt} complex, once thought by Werner to be isomeric with the analogous paramagnetic green compound mentioned above, and found it to be diamag-

netic and transformable by one-electron oxidation to the green form. Furthermore, they found that the red form contains one molecule of acid per dicobalt complex, and thereby accounted for the fact that both green and red compounds had the same number of anions (*e.g.*, four univalent anions) per binuclear complex cation in spite of the difference in the oxidation states.

The present study has unveiled further complications in the relation between compounds of this series, as well as among the corresponding ammonia complexes. Specifically, kinetic and equilibrium studies of the interchange between these compounds made it evident that a certain kind of isomerism also is intermingled with the redox and protonation phenomena. A short description of these studies has appeared elsewhere.[5]

Results and Discussion

I. On the Constitution of the Dibridged Peroxo–Dicobalt–Ethylenediamine Complexes. Although Thompson and Wilmarth inferred that Werner's red dibridged peroxo–dicobalt–ethylenediamine complex

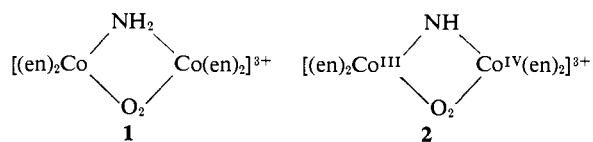(1) Based on work performed under the auspices of the U. S. Atomic Energy Commission.

(2) (a) A. Werner, *Ann.*, 375, 1 (1910); (b) L. Malatesta, *Gazz. Chim. Ital.*, 72, 287 (1942).

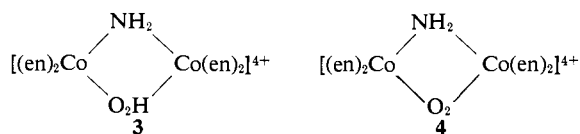(3) E. A. V. Ebsworth and J. A. Weil, *J. Phys. Chem.*, 63, 1890 (1959).

(4) L. R. Thompson and W. K. Wilmarth, *ibid.*, 56, 5 (1952).

(5) M. Mori and J. A. Weil, *Chem. Commun.*, 534 (1966).

was the acidic nitrate of the diamagnetic ion **1**, they did not actually isolate a neutral nitrate of this complex

$$[(en)_2Co\diagdown_{O_2}^{NH_2}Co(en)_2]^{3+} \qquad [(en)_2Co^{III}\diagdown_{O_2}^{NH}Co^{IV}(en)_2]^{3+}$$

$$\textbf{1} \qquad\qquad\qquad \textbf{2}$$

ion. On the other hand, Werner[2a] reported the existence of a brown salt which he formulated as an imido-bridged complex of type **2**, and which was prepared both from (what is now known as) the red acidic complex **3** and from the green paramagnetic ion **4** merely

$$[(en)_2Co\diagdown_{O_2H}^{NH_2}Co(en)_2]^{4+} \qquad [(en)_2Co\diagdown_{O_2}^{NH_2}Co(en)_2]^{4+}$$

$$\textbf{3} \qquad\qquad\qquad \textbf{4}$$

by addition of ammonia. The present authors isolated a brown normal nitrate fitting the formula **5** by adding

$$\left[(en)_2Co\diagdown_{O_2}^{NH_2}Co(en)_2\right](NO_3)_3\cdot2.5H_2O$$

$$\textbf{5}$$
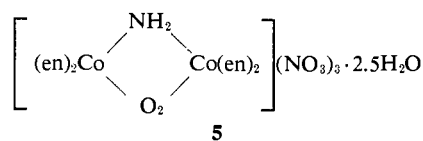
acetone to a brown solution obtained by treating either the red complex or the green complex with aqueous ammonia (preparation II; the cation of this compound is labeled B′ in later sections), and in all likelihood this is the same brown salt which Werner obtained, although he gave an analytical composition only for the iodide and double nitrate with silver nitrate. This very stable brown compound was diamagnetic, with mass susceptibility $\chi_g = -0.375 \times 10^{-6}$ cgs at 20°, and contained no paramagnetic ion detectable by epr spectroscopy at room temperature. It is oxidized immediately to the green paramagnetic complex when brought into an acidic solution of $(NH_4)_2$-$Ce(NO_3)_6$ or into moderately concentrated nitric acid. Thus

$$[(en)_2Co\diagdown_{O_2}^{NH_2}Co(en)_2]^{3+} \longrightarrow [(en)_2Co\diagdown_{O_2}^{NH_2}Co(en)_2]^{4+} + e^-$$

$$(1)$$
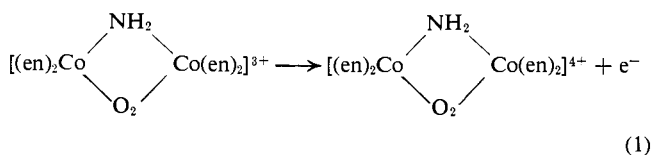
Werner's formulation of a system of type **2** for the brown ion implies the existence of an unpaired electron, contrary to our observation. It postulates the existence of the imido bridge without adequate data capable of distinguishing it from the amido bridge. Furthermore, the amido bridge in practice is remarkably stable, surviving even removal of the peroxo bridge and its replacement by other bridges such as NO_2. The presence of the "imido" complexes is even more difficult to rationalize in the complete absence of reports by Werner describing the expected analogous diamagnetic amido series.

We conclude therefore that Werner's imido complexes are in fact amido compounds, representing the actual diamagnetic counterparts of the paramagnetic dibridged ions. On the other hand, evidence will be presented in later sections that the red so-called acid nitrate of Werner and of Thompson and Wilmarth

is not just a simple protonated form of this diamagnetic counterpart.

II. On the Diamagnetic Peroxo–Dicobalt Complexes in Acids. In view of the tendency for the diamagnetic peroxo–dicobalt complexes to precipitate as acid salts, Thompson and Wilmarth[4] inferred that a proton might reside on the peroxo bridge in such salts. This idea was utilized by several authors[6–8] for interpretation of the decomposition and reduction of the diamagnetic peroxo–dicobalt–ammine complexes in acids.

In fact, we now know that the normal salt of diamagnetic ion **1** is brown while its acidic salt is red, and it seems quite reasonable to consider that the red color is that of the protonated cation. Similarly, it was reported by Vortmann[9] that the brown monobridged μ-peroxo-bis(pentaamminecobalt)(4+) complexes form unstable red salts on addition of acids. We have corroborated these results by isolating an acid salt describable formally either as μ-peroxo-bis(pentaamminecobalt)(4+) tetrabisulfate or as μ-hydroperoxo-bis-(pentaamminecobalt)(5+) trihydrogen tetrasulfate (preparation IV). In view of the color change of the cation, it is most probably true here also that (at least) one proton resides on the peroxo bridge; the optical spectrum is discussed in section V. The red compound is moderately stable at room temperature in a desiccator, but decomposes instantly in water or basic solution. It is insoluble in 6 M nitric acid and is rapidly oxidized to the paramagnetic 5+ ion by adding it to a slightly acidic solution containing ammonium persulfate.

We shall hereafter use the nomenclature μ-hydroperoxo for the acidic salts in the sense that the proton here is one of the constituents of the complex cation rather than simply filling the space in the lattice or binding to the anion. Also, the Ewens–Bassett System[10] of denoting the charge of the aggregate cation as above will be used because it does not seem reasonable to assign quadrivalence to one or the other of the cobalt atoms; the odd electron undoubtedly exists with a fairly large fraction of its orbital on the peroxo bridge.
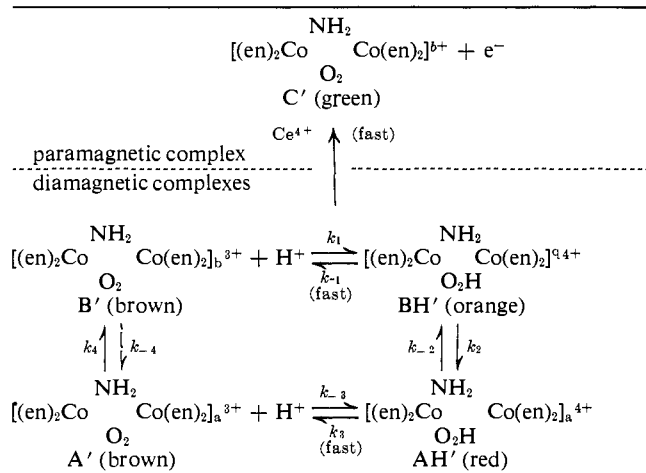
It was in an attempt to change the brown μ-amido-μ-peroxo-bis{bis(ethylenediamine)cobalt}(3+) compound described in section I above to the red acidic compound, and *vice versa*, that the authors met with the new complication: both processes were found to proceed at measurable rates. This is anomalous since most of the processes of protonation and acid dissociation are known to proceed very fast. It was also found that while the oxidation of the brown (3+) ion in acid solution proceeds immeasurably fast, the red acid salt is oxidized to the same (4+) ion only slowly. These findings suggested the existence of an unknown feature in the reaction system of these compounds and called for more detailed kinetic studies.

III. The Reaction Scheme of the μ-Amido-μ-peroxo-bis{bis(ethylenediaminecobalt)} Complexes. The results of the rate and equilibrium studies, details of which will

(6) W. Jakob and M. Ogorzalek, *Roczniki Chem.*, **30**, 1055 (1956).

(7) R. G. Charles and S. Barnartt, *J. Inorg. Nucl. Chem.*, **22**, 69 (1961).

(8) A. G. Sykes, *Trans. Faraday Soc.*, **58**, 543 (1962); **59**, 1325 (1963).

(9) G. Vortmann, *Monatsh.*, **6**, 404 (1885).

(10) "Definitive Rules for Nomenclature of Inorganic Chemistry," *J. Am. Chem. Soc.*, **82**, 5529, 5540 (1960).

be given in the succeeding sections, seem to be best understood by assuming the reaction scheme summarized in Table I. The suffixes b and a and the labels B′, BH′, AH′, and A′ are used in the sense that B′ is the only stable form in basic solution or in neutral salts, while AH′ is more stable than BH′ when found in acidic salts. The primes are attached to labels for en compounds to reserve unprimed letters for the corresponding ammine complexes.

Table I. Reaction Scheme of
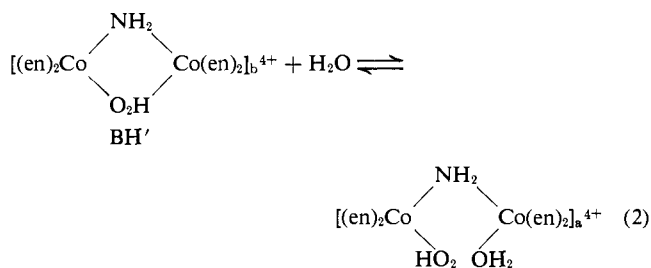μ-Amido-μ-peroxo-bis(bisethylenediaminecobalt) Ions

$$[(en)_2Co \overset{NH_2}{\underset{O_2}{}} Co(en)_2]^{5+} + e^-$$

C′ (green)

$$\text{Ce}^{4+} \uparrow \text{(fast)}$$

paramagnetic complex
diamagnetic complexes

$$[(en)_2Co \overset{NH_2}{\underset{O_2}{}} Co(en)_2]_b{}^{3+} + H^+ \underset{\underset{(fast)}{k_{-1}}}{\overset{k_1}{\rightleftharpoons}} [(en)_2Co \overset{NH_2}{\underset{O_2H}{}} Co(en)_2]^{q4+}$$

B′ (brown)   BH′ (orange)

$$k_4 \uparrow \downarrow k_{-4} \qquad k_{-2} \uparrow \downarrow k_2$$

$$[(en)_2Co \overset{NH_2}{\underset{O_2}{}} Co(en)_2]_a{}^{3+} + H^+ \underset{\underset{(fast)}{k_3}}{\overset{k_{-3}}{\rightleftharpoons}} [(en)_2Co \overset{NH_2}{\underset{O_2H}{}} Co(en)_2]_a{}^{4+}$$

A′ (brown)   AH′ (red)

The trivalent ion B′ is the brown diamagnetic dibridged en complex ion discussed in section I (preparation II), and A′ is considered to be an unstable isomer of B′. Likewise the protonated complexes BH′ and AH′ are considered to be isomeric to one another, but here both forms are considered to be present at equilibrium in solution. Whereas the conversions B′ ⇌ BH′ and A′ ⇌ AH′ are considered to proceed instantaneously, i.e., at rates immeasurably fast by conventional techniques, the conversions A′ → B′ and AH′ ⇌ BH′ proceed at measurable rates. In the scheme of Table I, Werner's red salt (compound V as cited in Thompson and Wilmarth's paper[4]) is represented by the nitrate of AH′ instead of the simple protonated version of the diamagnetic dibridged complex B′ as was assumed in the past (it should be noted that in the discussion following ref 4, there is mentioned the existence of two acidic complexes, which may possibly be our BH′ and AH′). Isolation of salts of complex ions A′ and BH′ has not been possible, but evidence for their existence will be presented in later sections of this work.

The above scheme not only explains qualitatively why the brown diamagnetic ion (B′) is oxidized immediately to the green complex ion (C′), whereas Werner's red ion is oxidized to the same complex ion with a slower measurable rate, but also it permits quantitative explanation of the coincidence of such an oxidation rate with that of the rate of conversion, k_{-2}, as well as a successful interpretation of the acid dependence of the conversion rate, as will be discussed later.

The possibility that the conversion BH′ ⇌ AH′ might in reality be a hydration–dehydration reaction

such as (2) seems to be excluded by a dehydration experiment. Initial attempts to dehydrate the powdered

$$[(en)_2Co \overset{NH_2}{\underset{O_2H}{}} Co(en)_2]_b{}^{4+} + H_2O \rightleftharpoons$$

BH′

$$[(en)_2Co \overset{NH_2}{\underset{HO_2 \quad OH_2}{}} Co(en)_2]_a{}^{4+} \quad (2)$$

red nitrate dihydrate of AH′ were unsuccessful because it was found that heating under high vacuum sufficiently (70°) to remove all the water caused simultaneous loss of water and nitric acid, with change in color to brown. However, it was possible to work with the AH′ bromide monohydrate first reported by Werner, et al.;[2a] he later described isolation of optically active red anhydrous bromide.[11] The racemic monohydrate was prepared by a somewhat different method in the present study (preparation IIIb). Heating powdered samples of this compound to constant weight under high vacuum at 57° gave the red anhydrous bromide of AH′, as ascertained by studies comparing the optical absorbance at the moment of dissolution, and the rates of conversion to B′ of the monohydrate and anhydrous forms.

IV. The Rate Equations of the Reaction System. The set of rate differential equations related to the reaction system in Table I is given in eq 3, where the

$$d[B′]/dt = -k_1[H][B′] + k_{-1}[BH′] - k_{-4}[B′] + k_4[A′] \tag{3a}$$

$$d[BH′]/dt = -k_{-1}[BH′] + k_1[H][B′] - k_2[BH′] + k_{-2}[AH′] \tag{3b}$$

$$d[AH′]/dt = -k_{-2}[AH′] + k_2[BH′] - k_3[AH′] + k_{-3}[H][A′] \tag{3c}$$

$$d[A′]/dt = -k_{-3}[H][A′] + k_3[AH′] - k_4[A′] + k_{-4}[B′] \tag{3d}$$

quantities [X] denote the concentrations at time t. Solving these equations is greatly facilitated by assuming perpetual existence of the acid–base equilibria

$$[B′][H] = k_{-1}/k_1[BH′]$$

$$[A′][H] = k_3/k_{-3}[AH′] \tag{4}$$

since $k_{-1}, k_1, k_3, k_{-3} \gg k_2, k_{-2}, k_4, k_{-4}$. The differential equation pertaining to [B′] and [H] with this assumption is (5), where $C_0 = [B′] + [BH′] + [A′] +$

$$(k_{-1} + k_1[H])(k_3 + k_{-3}[H]) \frac{d[B′]}{dt} +$$

$$k_1(k_3 + k_{-3}[H])[B′] \frac{d[H]}{dt} +$$

$$\{(k_3 + k_{-3}[H])(k_{-1}k_{-4} + k_1k_2[H]) +$$

$$(k_{-1} + k_1[H])(k_3k_4 + k_{-2}k_{-3}[H])\}[B′] -$$

$$k_{-1}(k_{-2}k_{-3}[H] + k_3k_4)C_0 = 0 \tag{5}$$

(11) A. Werner, H. Kuh, and P. Wüst, Ber., 47, 1975 (1914).

[AH']. Differential equations for $d[BH']/dt$, $d[AH']/dt$, and $d[A']/dt$ are analogous to (5). The solutions of these equations have different forms depending upon the conditions imposed on the system.

For a buffered system in which $d[H]/dt = 0$, the solutions become simple; each concentration approaches its equilibrium value exponentially with the pseudo-first-order rate constant given in (6). The solution

$$k_{ps} = \frac{k_{-1}k_{-4} + k_1k_2[H]}{k_{-1} + k_1[H]} + \frac{k_3k_4 + k_{-2}k_{-3}[H]}{k_3 + k_{-3}[H]} \quad (6)$$

without the assumption of acid–base equilibria 4 contains an extra exponential term which acts sufficiently rapidly that it can be neglected in the time scale of our experiments. The situation is the same for the time dependence of the absorbances, derived later.

In order that, at the final equilibrium, the equations

$$[AH']_\infty = (k_2/k_{-2})[BH']_\infty$$

$$[A']_\infty = (k_{-4}/k_4)[B']_\infty \quad (7)$$

should hold in addition to (4), an extra condition

$$k_1k_2k_3k_4 = k_{-1}k_{-2}k_{-3}k_{-4} \quad (8)$$

must hold for the rate constants. The equilibrium concentrations are then as shown in eq 9.

$$[B']_\infty = \frac{k_{-1}k_{-2}k_{-3}C_0}{k_1k_2(k_3 + k_{-3}[H]) + k_{-2}k_{-3}(k_{-1} + k_1[H])} \quad (9a)$$

$$[BH']_\infty = \frac{k_1k_{-2}k_{-3}[H]C_0}{k_1k_2(k_3 + k_{-3}[H]) + k_{-2}k_{-3}(k_{-1} + k_1[H])} \quad (9b)$$

$$[AH']_\infty = \frac{k_1k_2k_{-3}[H]C_0}{k_1k_2(k_3 + k_{-3}[H]) + k_{-2}k_{-3}(k_{-1} + k_1[H])} \quad (9c)$$

$$[A']_\infty = \frac{k_1k_2k_3C_0}{k_1k_2(k_3 + k_{-3}[H]) + k_{-2}k_{-3}(k_{-1} + k_1[H])} \quad (9d)$$

As will be seen in later sections, the relevant orders of magnitude are $k_{-1}/k_1 \sim 1$, $k_2 \sim 10^{-2}$, $k_{-2} \sim 10^{-2}$, $k_3/k_{-3} \sim 10^{-11}$, $k_4 \sim 10^{-1}$. Equation 8 then requires that $k_{-4} \sim 10^{-12}$, which is effectively zero as a rate constant. That this is in fact the case was attested to by the invariance of the optical spectrum of B' when dissolved in alkaline solution.

The pseudo-first-order rate constant in acidic solution is to a good approximation

$$k_a = \frac{k_1k_2[H]}{k_{-1} + k_1[H]} + k_{-2} \quad (6a)$$

since $k_{-3}[H] \gg k_3$. In alkaline solution the pseudo-first-order rate constant may be expressed as

$$k_b = \frac{k_3k_4 + k_{-2}k_{-3}[H]}{k_3 + k_{-3}[H]} = \frac{k_3k_4 - k_{-2}k_3}{k_3 + k_{-3}[H]} + k_{-2} \quad (6b)$$

since $k_1[H] \ll k_{-1}$.

Since most of the rate study was made by optical measurements, some expressions for the absorbances must also be presented here. We define the average

molar absorptivity of a solution containing B', BH', AH', and A' by (10), where $\bar{A}$ is the absorbance

$$\bar{\epsilon} = \bar{A}/C_0 = (\epsilon_{B'}[B'] + \epsilon_{BH'}[BH'] + \epsilon_{AH'}[AH'] + \epsilon_{AH'}[A'])/C_0 \quad (10)$$

of the solution, $\epsilon_{B'}$ is the molar absorptivity of B', etc., and C_0 is the total concentration as before.

In a buffered system, [X] has the time dependence, $[X] = [X]_\infty + ([X]_0 - [X]_\infty) \exp(-k_{ps}t)$, so that in this case

$$\bar{\epsilon} = \bar{\epsilon}_\infty + (\bar{\epsilon}_0 - \bar{\epsilon}_\infty) \exp(-k_{ps}t) \quad (11)$$

where $\bar{\epsilon}_\infty$ is defined in eq 12. In case pure B' is dissolved at the start of the reaction, then $[B']_0 + [BH']_0 = C_0$ and $[B']_0 = k_{-1}C_0/(k_{-1} + k_1[H])$; $[BH']_0 = k_1[H]C_0/(k_{-1} + k_1[H])$, and it can be readily seen that

$$\bar{\epsilon}_\infty = \frac{k_{-1}k_{-2}k_{-3}\epsilon_{B'} + k_1k_{-2}k_{-3}[H]\epsilon_{BH'} + k_1k_2k_{-3}\epsilon_{AH'} + k_1k_2k_3[H]\epsilon_{A'}}{k_1k_2(k_3 + k_{-3}[H]) + k_{-2}k_{-3}(k_{-1} + k_1[H])} \quad (12)$$

$$\bar{\epsilon}_0 = \frac{k_{-1}\epsilon_{B'} + k_1[H]\epsilon_{BH'}}{k_{-1} + k_1[H]} \quad (13)$$

The solution of (5) for the unbuffered system is rather complex. When no extra acid or base is present, and when species A' may be ignored under the assumption that $k_{-3}[H] \gg k_3$, i.e., in nonbasic solution, the solution becomes

$$z_t \left\{ \frac{k_{-1}k_{-2} + k_1(k_2 + k_{-2})[H]_\infty(2 - z_t)}{k_{-1}k_2 + k_1(k_2 + k_{-2})[H]_\infty} \right\}^p =$$
$$\exp\left\{ -k_{-2}\left(1 + \frac{2k_1k_2[H]_\infty}{k_{-1}k_{-2} + 2k_1k_{-2}[H]_\infty}\right)t \right\} \quad (14)$$

where

$$p = \exp\left(\frac{k_{-1}k_{-2} + 2k_1(k_2 + k_{-2})[H]_\infty - k_2}{k_{-1}k_{-2} + 2k_1(k_2 + k_{-2})[H]_\infty + k_2}\right)$$

$$z_t = \frac{[B']_\infty - [B']}{[B']_\infty} = \frac{[H]_\infty - [H]}{[H]_\infty}$$

$$\frac{[BH']_\infty - [BH']}{[BH']_\infty} = z_t(2 - z_t)$$

$$\frac{[AH']_\infty - [AH']}{[AH']_\infty - [AH']_0} = z_t \frac{k_{-1} + k_1[H]_\infty(2 - z_t)}{k_{-1} + k_1[H]_\infty} \quad (15)$$

and where we assumed that only AH' was present initially, i.e., $[AH']_0 = C_0$, $[BH']_0 = [B']_0 = [H]_0 = 0$, and $[B'] = [H]$.

Before presenting the actual kinetic data, some aspects of absorption spectra of the related complexes will be described in the next section.

V. On the Optical Spectra of the Complexes. The absorption spectra of the μ-amido-μ-peroxo-en-dicobalt complexes in aqueous solution are shown in Figure 1. The ions AH' and BH' exist only in the mixed state when at equilibrium, so that the spectra of these ions were actually obtained by the extrapolation method in the kinetic and equilibrium studies. Figure 2 shows the reflection powder spectra of the corresponding nitrates diluted to 1:5 in weight by potas-
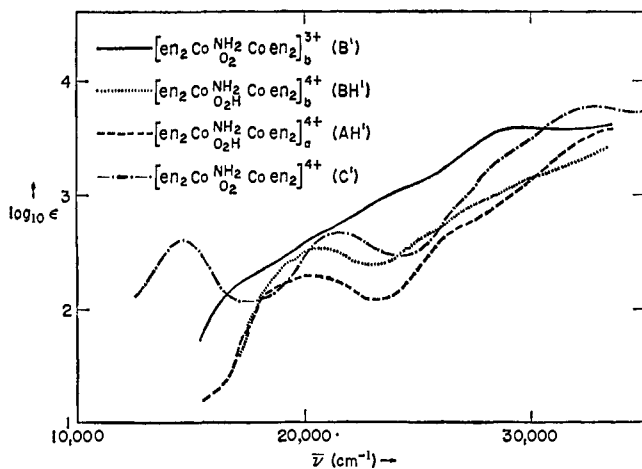
Figure 1. Optical absorption spectra of several dibridged dicobalt-en complexes in water.

Figure 2. Optical reflection spectra of several dibridged dicobalt-en complexes in powdered K_2SO_4.

sium sulfate. The quantity $\log(1 - R_d)^2/2R_d$, where R_d = diffuse reflectance (cf. Experimental Section), is plotted in the figure since $(1 - R_d)^2/2R_d$ is known to be proportional to ϵ in many cases.[12]

Both absorption and reflection spectra show clear distinction between the spectra of the diamagnetic, the protonated diamagnetic, and the paramagnetic complexes. There is excellent agreement between peak positions of the same ionic species in these two types of spectra (Table II). We note that the optical spectrum given by Thompson and Wilmarth (ref 4, Figure 1) is actually that of B' rather than AH'; we confirm the presence of the small shoulder at 337 mμ observed by them.

Table II. Peaks in Absorption and Reflection Spectra of Peroxo-Dicobalt-Ammine Complexes

Ions	Absorption spectra of soln $\bar{\nu}$, cm^{-1}	Log ϵ	Reflection spectra of powder $\bar{\nu}$, cm^{-1}
NH$_2$			
[(en)$_2$Co Co(en)$_2$]$_b$$^{3+}$	16,800 (sh)	2.17	16,700 (sh)
O$_2$	29,700	3.59	28,600
NH$_2$			
[(en)$_2$Co Co(en)$_2$]$_b$$^{4+}$	20,500	2.54	
O$_2$H			
NH$_2$			
[(en)$_2$Co Co(en)$_2$]$_a$$^{4+}$	20,350	2.30	20,300^a
O$_2$H			
NH$_2$	14,600	2.60	14,700
[(en)$_2$Co Co(en)$_2$]$^{4+}$	21,600	2.67$_5$	21,400
O$_2$	32,800	3.78	
[(NH$_3$)$_5$CoO$_2$Co(NH$_3$)$_5$]$^{4+}$			15,000 (sh)
[(NH$_3$)$_5$CoO$_2$HCo(NH$_3$)$_5$]$^{5+}$			20,100^a
[(NH$_3$)$_5$CoO$_2$Co(NH$_3$)$_5$]$^{5+}$	14,900	2.91$_5$	15,200
	21,200	2.41	20,650

^{a} The peak at 15,000 cm^{-1} is doubtless due to contamination by the paramagnetic salt.

The spectra of AH' and BH' are similar in shape, but the difference in the absorptivity values at the absorption minimum of AH' at 435 mμ (=23,000 cm^{-1}; $\epsilon_{AH'}$ 110, $\epsilon_{BH'}$ 250, $\epsilon_{B'}$ 830, cf. section VI-C) was sufficient to allow precise kinetic and equilibrium studies

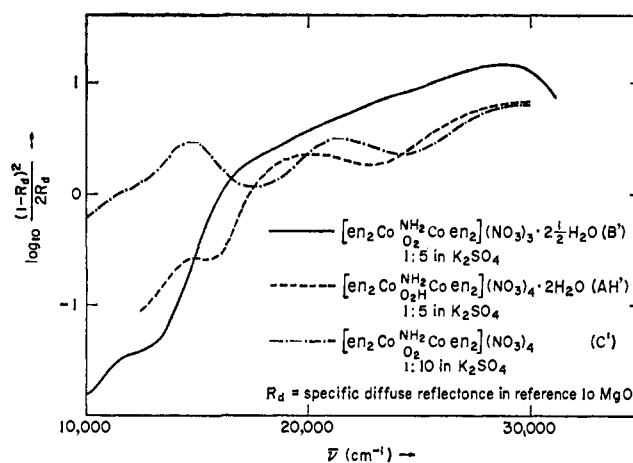(12) G. Kortüm and H. Schöttler, Z. Elektrochem., 57, 353 (1953).

as discussed in section VI. For the determination of the oxidation rate k_{OX} of AH' → C', the wavelength of one of the absorption peaks of C' (687 mμ = 14,550 cm^{-1}, $\epsilon_{AH'}$ 400) was utilized; C' is the cation in [(en)$_2$Co(NH$_2$)(O$_2$)Co(en)$_2$](NO$_3$)$_4$. The absorbance of the Ce(IV) complex used as the oxidant is negligibly small at this wavelength. The value of $\epsilon_{AH'}$ at 687 mμ obtained as the limiting absorbance at $t = 0$ in the kinetic study fell close to 10, but it has been difficult to determine its exact value because of slight contamination with C' (1% contamination would raise ϵ by 4). However, use of such samples in the kinetic study should not affect the value of k obtained because d $\log(\epsilon_\infty - \epsilon_t)/dt$ is unaffected by the presence of C' initially. The excellent agreement between k_{OX} and k_{-2} (cf. sections III and VII) proves the validity of this assumption, as well as the absence of any effect on the rate of the difference in illumination (daylight vs. 687-mμ light).

Solutions of the oxidized complex C' in acid solutions of various concentrations up to 11 N in perchloric acid and up to 33 N in sulfuric acid gave spectra indistinguishable from the spectrum of C' in plain water shown in Figure 1, proving the low tendency of the oxidized complex toward protonation, since it is unlikely that C' is already protonated in water (the solutions test neutral) or that a protonated species would have the same spectrum as the unprotonated one. This constancy is not inconsistent with variation of the epr spectrum, which undergoes considerable change in line width and in the degree of asymmetry when the acid concentration is changed, since neither the g value nor the cobalt hyperfine splitting is altered in this process.[3]

The reflection spectra of μ-peroxo-bis(pentaamminecobalt) single-bridged complexes are given in Figure 3. The general trend of the change of the spectra caused by oxidation and acid salt formation is very similar to that in the preceding case of μ-amido-μ-peroxo-en complexes. This proves the occurrence of the protonated diamagnetic ion even in this monobridged series, although this protonated ion was shown to be very unstable in aqueous solutions.

VI. A. Measurement of k_{-2} of Reaction AH' → BH'. We first consider the case in which AH' is dissolved in pure water or an aqueous solution of sodium
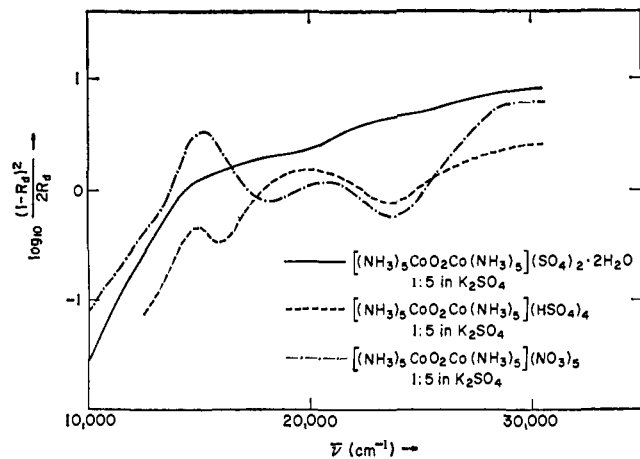
Figure 3. Optical reflection spectra of several monobridged dicobalt–ammine complexes in powdered K_2SO_4.

perchlorate. Equation 14 is the relevant rate equation for this situation. The initial time dependence of the solution is shown by expansion to be

$$[AH']/[AH']_0 = \exp(-k_{-2}t) \qquad (14a)$$

The final dependence is

$$z_t = \frac{[B']_\infty - [B']}{[B']_\infty} =$$

$$\exp\left\{-k_{-2}\left(1 + \frac{2k_1k_2[H]_\infty}{k_{-1}k_{-2} + 2k_1k_{-2}[H]_\infty}\right)t\right\} \qquad (15a)$$

In our experimental conditions, $[H]_\infty = C_0 \sim 0.001$ and $k_{-1}/k_1 \geq 0.1$, so that the time dependence to a good approximation (within ca. 1%) is that of a first-order reaction with rate constant k_{-2}. This situation arises from the fact that BH' is a strong acid and is almost completely dissociated to B' and H+ as soon as it is formed from AH'. Table III presents k_{-2} determined

Table III. Rate Constants k_{-2} (sec^{-1}) of Conversion AH' $\longrightarrow$ BH', and k_{ox} of Oxidation, AH' $\longrightarrow$ C'

Temp, °C	k_{-2} in Water	0.106 M NaClO₄ (aq)	0.265 M NaClO₄ (aq)	k_{-2} av	k_{ox} in HClO₄ (aq)^a
4.93	0.00430	. . .	0.00429	0.00430	0.00436
9.92	0.00827	0.00825	0.00825	0.00826	0.00821
14.85	0.0154	0.0153	0.0158	0.0155	0.0157
19.93	0.0293	0.0293	0.0296	0.0294	0.0294^b
24.92	0.0523	0.0523	0.0529	0.0525	0.0525

^{a} Containing Ce^{4-}. ^{b} Average of values in Table IV.

in this way by use of the change of absorbance at 435 mμ (Table III also gives the rate constant k_{ox} of oxidation of AH' to C', as explained in section VII). The reason why k_{-2} was determined in unbuffered solutions is that the usual buffers (phosphates, borates, phthalates) affected the measured rates and/or absorbances, probably due to complexing reactions. The values of k_{-2} measured in solutions with various concentrations of sodium perchlorate are independent of ionic strength. This result suggests that the activated complex has the same ionic charge as AH' (see also Table IV for k_{ox} values).
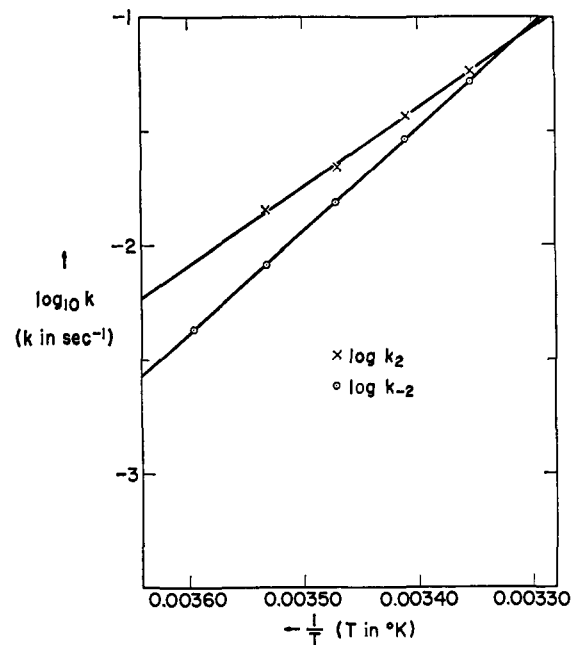

Figure 4. Arrhenius plots for the rate constants k_2 and k_{-2} of the reaction BH' $\rightleftharpoons$ AH' in acidic solution.

Table IV. Rate Constant k_{ox} of Oxidation AH' $\longrightarrow$ C' in Different Concentrations of Oxidant and Acid (19.93°)

Complex AH'	Initial concentration, M (NH₄)₂-Ce(NO₃)₆	HClO₄	k_{ox}, sec^{-1}
0.001436	0.00959	0.053	0.0298
0.001360	0.00959	0.106	0.0296
0.001404	0.00480	0.0265	0.0291
0.001280	0.00480	0.106	0.0292
0.001301	0.00174	0.053	0.0295
		Average	0.0294

The plot of log k_{-2} vs. the reciprocal of the absolute temperature in Figure 4 shows an excellent linearity, and by linear fitting with a computer using eq 16a and 16b, the Arrhenius energy of activation $(E_{act})_{-2}$, the

$$\ln k = \ln \nu - E_{act}/RT \qquad (16a)$$

$$\ln \nu = \ln (kT/h) + (\Delta S^\ddagger/R) + 1 \qquad (16b)$$

frequency factor ν_{-2}, and the entropy of activation $\Delta S^\ddagger_{-2}$ of the reaction AH' $\rightarrow$ BH' were found to be given by $(E_{act})_{-2} = 20.7 \pm 0.1$ kcal/mole, log $\nu_{-2} = 13.9 \pm 0.1$ (ν in sec^{-1}), $\Delta S^\ddagger_{-2} = 3 \pm 1$ eu.

B. Measurement of k_2 and K_1 by Use of Kinetic Absorbance Data. Next we consider the situation when a dilute solution of BH' is acidified with enough acid to keep the hydrogen ion concentration approximately constant. In this case the equilibrium B' + H+ $\rightleftharpoons$ BH' $\rightleftharpoons$ AH' will be reached with the pseudo-first-order rate constant k_a given by eq 6a in section IV. Since the measurement of pH is based on the measurement of emf, the quantity obtained should be more directly related to the hydrogen ion activity a_H than to the true concentration [H]. In this sense, it is advisable to adapt the equation to apply to a_H. At equilibrium, eq 17 holds, where the quantities a and f

$$K_1^0 = \frac{a_H a_{B'}}{a_{BH'}} = \frac{f_H f_{B'}}{f_{BH'}}\frac{[H][B']}{[BH']} \qquad (17)$$
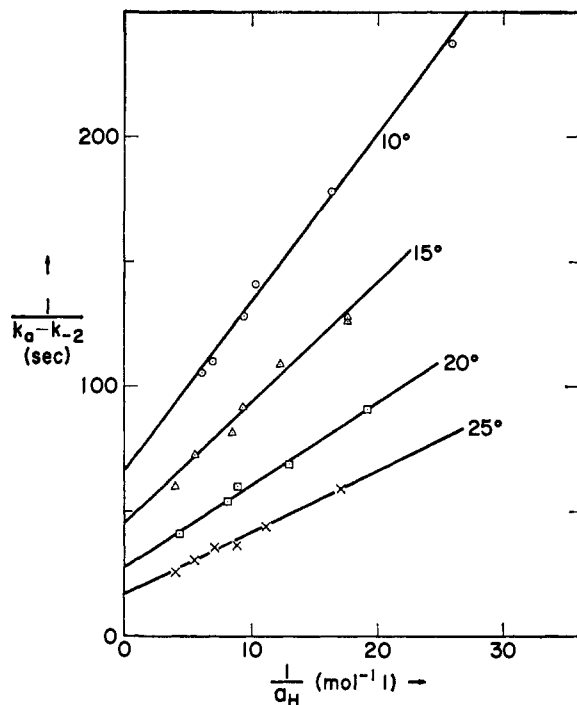
Figure 5. The dependence of $(k_a - k_{-2})^{-1}$ on the reciprocal of the hydrogen ion concentration in acidic solution, at several temperatures.

are activities and activity coefficients, respectively. Since it is common practice to define rate constants in terms of concentrations as rate $(B' \rightarrow BH') \equiv k_1[B'][H]$, rate $(BH' \rightarrow B') \equiv k_{-1}[BH']$, the relationship between k_1, k_{-1}, and K_1^0 is evidently

$$\frac{k_{-1}}{k_1} = \frac{[H][B']}{[BH']} = \frac{f_{BH'}}{f_H f_{B'}} K_1^0 = \frac{K_1}{f_H} \qquad (18)$$

where K_1 is just the "uncorrected" equilibrium constant in the usual sense. By use of K_1 as defined above, the rate equation (6a) becomes

$$k_a = \frac{a_H}{a_H + K_1} k_2 + k_{-2} \qquad (6a')$$

or

$$\frac{1}{k_a - k_{-2}} = \frac{1}{k_2} + \frac{K_1}{k_2 a_H} \qquad (6a'')$$

Thus if the pseudo-first-order rate constant k_a is measured at different pH values, the plot of $(k_a - k_{-2})^{-1}$ against a_H^{-1} should give a straight line. This is actually the case, as indicated by the plots presented in Figure 5 derived from such kinetic studies at various temperatures, again by use of the optical absorption at 435 mμ. In this series of experiments, the concentration of the perchloric acid was varied from 0.05 to 0.239 M, while the concentration of the complex was 0.001 M, and by addition of sodium perchlorate the total concentration of the perchlorate ion was kept at 0.239 M, thus resulting in an ionic strength $s = 0.245$. The values of k_{-2} used in the calculation are already known from the study of the backward reaction discussed in section VI-A. Values of K_1 and k_2 are thus obtained from the intercept and the slope of Figure 5. Table V summarizes such data as worked out by a linear fitting program.

Table V. Rate Constant k_2 and Equilibrium Constant K_1 as Obtained from Plots of $(k_a - k_{-2})^{-1}$ vs. a_H^{-1} (Ionic Strength = 0.245)

Temp, °C	k_2 from intercept	K_1 from slope and intercept	pK_1
10	0.015 ± 0.001	0.101 ± 0.008	0.99 ± 0.08
15	0.022 ± 0.002	0.105 ± 0.015	0.98 ± 0.14
20	0.036 ± 0.003	0.121 ± 0.016	0.91 ± 0.13
25	0.059 ± 0.005	0.147 ± 0.020	0.84 ± 0.14

Since the plots in Figure 5 are indeed linear with the first power of a_H^{-1} at least up to acidity of pH 0.6, we can deduce that but a single proton is added to the cobalt complex B' in the process B' → BH'. It should also be noted here that eq 6a, etc., apply also to the case when AH' is dissolved in an acidic solution of constant pH, approaching an equilibrium mixture of AH', BH', and B'. This was checked in a few such runs.

C. Measurement of k_2 and K_1 by Combined Use of Kinetic and Initial Absorbance Data. The above method of obtaining K_1 and k_2 is illustrative in that it tests the validity of our assumptions. However, it has a disadvantage in that both the intercept and the slope are affected greatly by even small errors in k_a values determined at low hydrogen ion concentration, where $(k_a - k_{-2})^{-1}$ is very large. For this reason the method is not applicable to the system with low ionic strength since here the acidity is automatically limited.

There is another and more usual way of obtaining K_1 when the acid form and the base form have different optical absorbances.[13] The problem here is slightly complicated because of the simultaneous occurrence of the isomerization reaction, so that one must use the absorbance of the solution immediately after mixing the solution of pure complex B' with acid. Fortunately, however, this quantity is readily obtained from the extrapolation to this time origin of the plot of log $(\bar\epsilon_t - \bar\epsilon_\infty)$ used for determination of k_a. The average molar absorptivity at time zero is given by eq 13 of section IV, or, in terms of K_1 and a_H

$$\bar\epsilon_0 = \frac{K_1 \epsilon_{B'} + a_H \epsilon_{BH'}}{K_1 + a_H} \qquad (13a)$$

Parameter $\epsilon_{B'}$ can be directly measured as the molar absorptivity of B' in water and has the value $\epsilon_{B'} = 830$ at 435 mμ, while the value of $\epsilon_{BH'}$ should correspond to the value of $\bar\epsilon_0$ at the high acidity limit and was shown to have the value 250 as obtained in 6 and 12 N sulfuric acid. Both $\epsilon_{B'}$ and $\epsilon_{BH'}$ measured in this way were found to be independent of temperature ($\sim$10–25°) within the experimental error. Thus it is possible to evaluate pK_1 from $\bar\epsilon_0$ values at intermediate acidity (pH $\sim$ pK_1) and at a definite ionic strength by using the relation

$$pK_1 = pH + \log \frac{\epsilon_{B'} - \bar\epsilon_0}{\bar\epsilon_0 - \epsilon_{BH'}} \qquad (13b)$$

Values of $\bar\epsilon_0$ obtained from the same series of experiments (with $s = 0.245$) as discussed in section VI-B, and values of pK_1 calculated therefrom, are given in

(13) W. Stenström and N. Goldsmith, *J. Phys. Chem.*, **30**, 1683 (1926).

Table VI. Calculation of pK_1 and k_2 from Kinetic and Absorbance Data[a]

Temp, °C	pH	$\bar{\epsilon}_0$	$\dfrac{\epsilon_B - \bar{\epsilon}_0}{\bar{\epsilon}_0 - \epsilon_{BH'}}$[b]	pK_1	$1 + (K_1/a_H)$	$k_a - k_{-2}$, sec^{-1}	k_2, sec^{-1}
			a. Ionic Strength = 0.245				
10.0 ± 0.2	1.41	639	0.491	1.10	3.04	0.00421	0.0128
	1.21	588	0.716	1.06	2.40	0.00562	0.0135
	1.01	548	0.946	1.02	2.06	0.00709	0.0146
	0.97	521	1.140	1.03	1.88	0.00781	0.0147
	0.84	477	1.555	1.03	1.64	0.00908	0.0149
	0.78	447	1.944	1.07	1.51	0.00948	0.0144
			Average	1.05		Average	0.014
15.0 ± 0.2	1.25	624	0.551	0.99	2.81	0.0079	0.0222
	1.25	608	0.620	1.04	2.61	0.0078	0.0204
	1.09	570	0.813	1.00	2.23	0.0092	0.0205
	0.965	542	0.986	0.96	2.01	0.0109	0.0219
	0.93	539	1.007	0.93	1.99	0.0122	0.0243
	0.74	463	1.723	0.98	1.58	0.0137	0.0216
	0.60	433	2.169	0.94	1.46	0.0166	0.0242
			Average	0.98		Average	0.022
20.0 ± 0.1	1.28	657	0.425	0.91	3.35	0.0110	0.0368
	1.11	614	0.593	0.88	2.69	0.0145	0.0390
	0.95	555	0.902	0.90	2.11	0.0166	0.0350
	0.91	535	1.035	0.92	1.97	0.0185	0.0364
	0.64	466	1.685	0.87	1.59	0.0244	0.0388
			Average	0.90		Average	0.037
25.0 ± 0.1	1.23	668	0.388	0.82	3.58	0.0168	0.0601
	1.05	609	0.616	0.84	2.62	0.0226	0.0593
	0.95	575	0.784	0.84	2.27_6	0.0272	0.0619
	0.85	538	1.013	0.86	1.98_8	0.0278	0.0553
	0.76	496	1.359	0.89	1.73_6	0.0320	0.0556
	0.61	462	1.735	0.85	1.57_6	0.0369	0.0581
			Average	0.85		Average	0.058
			b. Ionic Strength = 0.102				
10.0 ± 0.2	1.40	703_5	0.279	0.85	4.58	0.00274	0.0125
	1.32	688	0.324	0.83	4.08	0.00380	0.0155
	1.20	640	0.454	0.86	3.20	0.00470	0.0150
	1.10	609_5	0.614	0.89	2.63	0.00516	0.0136
			Average	0.86		Average	0.014
15.0 ± 0.2	1.38	719	0.237	0.75	5.23	0.0032	0.0167_5
	1.30	692	0.312	0.79	4.20	0.0046	0.0193
	1.16	652	0.443	0.81	3.26	0.0063	0.0206
	1.03	627	0.546	0.77	2.83	0.0078	0.0222
			Average	0.78		Average	0.020
25.0 ± 0.1	1.40	731	0.206	0.71	5.86	0.0106	0.0621
	1.30	710	0.261	0.72	4.84	0.0120	0.0581
	1.11	664	0.401	0.71	3.49_5	0.0141	0.0493
	1.06	658	0.422	0.68	3.37	0.0199	0.0670
	1.02	628	0.535	0.75	2.87	0.0212	0.0608
			Average	0.71		Average	0.060
			c. Temperature 10 ± 0.2°				
Ionic strength 0.054	1.82	792	0.0701	0.67	15.26	0.00085	0.0130
	1.74	788	0.0781	0.63	13.80	0.00110	0.0152
	1.68	770	0.1153	0.74	9.67	0.00150	0.0145
	1.49	743	0.1766	0.74	6.66	0.00202	0.0134_5
	1.40	721	0.232	0.76	5.32	0.00247	0.0131_3
			Average	0.71		Average	0.014
0.030	2.01	808	0.0394	0.61	26.4		
	1.90	806	0.0431	0.53	24.2		
	1.775	793	0.0532	0.61	15.7		
	1.71	780	0.0943	0.68	11.6		
			Average	0.61			

[a] $\epsilon_{B'}$ 830, $\epsilon_{BH'}$ 250; 435 mμ. [b] $(\epsilon_{B'} - \bar{\epsilon}_0)/(\bar{\epsilon}_0 - \epsilon_{BH'}) = a_H/K_1$.

Table VIa and the fitting of the experimental values of $\bar{\epsilon}_0$ with the theoretical curves is shown in Figure 6; data at other values of ionic strength are included in Tables VIb and VIc.

Since eq 13a can be written as $(\bar{\epsilon}_0 - \epsilon_{BH'})/(\epsilon_{B'} - \bar{\epsilon}_0) = K_1/a_H$ where the right-hand term is exactly the slope term of eq 6a'', we can combine these data with $k_a - k_{-2}$ from the kinetic measurements to obtain k_2.
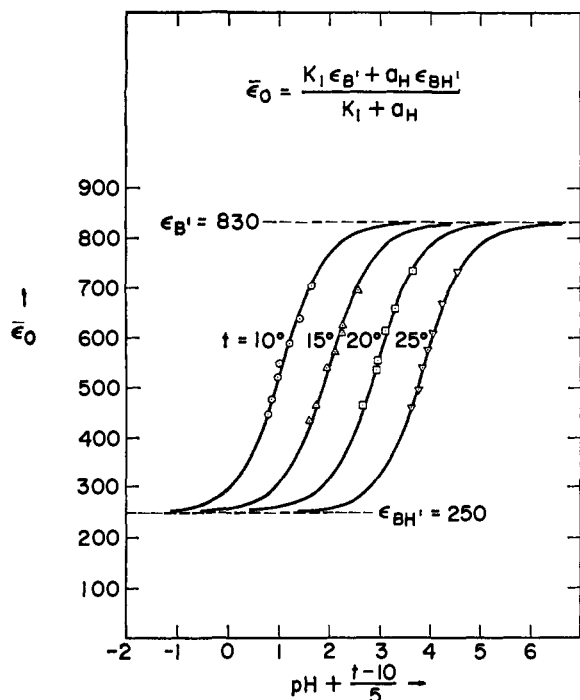
$$\bar{\epsilon}_0 = \frac{K_1 \epsilon_{B'} + a_H \epsilon_{BH'}}{K_1 + a_H}$$

Figure 6. The initial average molar absorptivity at 435 mμ, as a function of acidity, for mixtures of B' and BH' at various temperatures.

The values of k_2 thus obtained are listed in Tables VIa–c. (At ionic strength = 0.030, the difference $k_a - k_{-2}$ was too small to give any reliable k_2 values.) One advantage of this method, as compared to the linear fitting method in section IV, is that the ratio a_H/K_1 obtained in this manner is independent of the scale of the pH meter. Furthermore, the results do not depend too much on the k_a values at a low hydrogen ion concentration, where the measurement is inaccurate. Thus the data of pK_1 and k_2 in Table VIa are thought to be more reliable than those in Table V. It should be noted, however, that because of the difficulty of temperature control in the measurement of k_a (cf. Experimental Section), and also because of the extra steps of calculation involved, the accuracy of k_2 is poorer than that of k_{-2} (for AH' $\rightarrow$ BH', Table III), presumably by a factor of 10. Thus although Tables VIa–c suggest that k_2 is independent of the ionic strength, the constancy was not as clearly demonstrated as in the case of k_{-2}. On the other hand, K_1 does depend on the ionic strength, as is expected also from the theoretical considerations.

The plot of log k_2 vs. $1/T$ from values in Table VIa is shown in Figure 4, and the thermochemical data for BH' $\rightarrow$ AH' were worked out as: $(E_{act})_2 = 15.9 \pm 0.4$ kcal/mole, log $\nu_2 = 10.4 \pm 0.3$, $\Delta S^{\ddagger}_2 = -13 \pm 3$ eu (cf., similar data for k_{-2} in section VI-A).

If one takes the mean extinction $\bar{\epsilon}_\infty$ measured under true equilibrium conditions (i.e., after sufficiently long time) and follows a procedure analogous to that used in calculating pK_1 from $\bar{\epsilon}_0$, one arrives at the quantity $-\log \{K_1/(1 + K_2)\}$ instead of pK_1, as is readily proved by using eq 12. Thus log $(\epsilon_{B'} - \bar{\epsilon}_\infty)/(\bar{\epsilon}_\infty - \epsilon_{ABH'}) = -\log \{K_1/(1 + K_2)\}$, where $\epsilon_{ABH'} = (\epsilon_{BH'} + K_2\epsilon_{AH'})/(1 + K_2)$ is the average molar absorptivity of an equilibrium mixture of AH' and BH' at the high acidity limit. It is not easy to obtain $\epsilon_{ABH'}$ from ex-

periment because the complex ions decompose when in solutions of high acidity for a long time. However, it is possible to calculate $\epsilon_{ABH'}$ if we use $K_2 = k_2/k_{-2}$ from data in Table VI and assume $\epsilon_{BH'}$ 250 and $\epsilon_{AH'}$ 110 at 435 mμ. Table VII summarizes the results of such calculations. By use of the same K_2 values, p$K_1 = -\log K_1/(1 + K_2) - \log (1 + K_2)$ was also calculated. The last column contains pK_1 from Table VI, for comparison. The agreement is not very satisfactory, especially at 20 and 25°. This seems to be due to some side reactions which made the measured $\bar{\epsilon}_\infty$ lower, as was shown by a slow decrease of absorbance after the main reaction was virtually complete.

Table VII. The pK_1 Values Calculated from $\bar{\epsilon}_\infty$ as Compared to Those from $\bar{\epsilon}_0$ (Ionic Strength = 0.245)

Temp, °C	From Tables II and V $K_2 = k_2/k_{-2}$	Log $(1 + K_2)$	From $\bar{\epsilon}_\infty$ $-\log [K_1/ (1 + K_2)]$	pK_1	From $\bar{\epsilon}_0$ pK_1
10	1.72	0.434	1.46$_0$	1.03	1.05
15	1.43	0.38$_6$	1.37$_1$	0.99	0.98
20	1.27	0.35$_5$	1.32$_1$	0.97	0.90
25	1.11	0.32$_4$	1.23$_0$	0.91	0.85

The series of spectra measured at true equilibrium obtained at fixed temperature for various pH values shows isosbestic points[14] (at 240 and 267 mμ, 22°). This indicates that the system in equilibrium behaves as if it were composed of two components B' and "ABH'," where ABH' denotes an equilibrium mixture of AH' and BH' in the definite ratio K_2:1. It also indicates that no other ions participate in the system.

D. Correction of pK_1 for the Effect of Electrolytes. Although it is advisable to make pK determinations in solutions of sufficiently low ionic strength so that the linear relation between pK and $\sqrt{s}$ holds, this was not actually realizable because high acidity was required in experiments for evaluating values of pK_1 as low as 1.

According to the Debye–Hückel theory, the experimental pK_1 and the true one, pK_1^0 (cf. eq 18, section VI-B), are related by (19), where $\alpha = e^2/2(\ln 10)DkT$,

$$p K_1^0 = p K_1 + \log (f_{BH'}/f_{B'}) =$$

$$p K_1 + \frac{\alpha\beta\sqrt{s}}{1 + \beta r\sqrt{s}} (Z_{B'}^2 - Z_{BH'}^2) \quad (19)$$

$\beta = (8\pi Ne^2\rho/100DkT)^{1/2}$, r is the average distance of approach of ions at collision, N is the Avogadro number, T is the absolute temperature, e is the unit charge of electricity, ρ is the density of solution, D is the dielectric constant of water calculated from the empirical formula $D = D_0e^{-LT}$ (here $D_0 = 311.17$, $D_{298.16} = 78.54$),[15] and Z is the ionic charge (so that $Z_{B'}^2 - Z_{BH'}^2 = 7$). From the ionic strength dependence of pK_1 at 10° (Table VI), we evaluated r by minimizing the sum over $(pK_1^0 - \overline{pK_1^0})^2$, where p$K_1^0$ was calculated from (19) with $\alpha = 0.4959$ and $\beta = 0.3258$, and $\overline{pK_1^0}$ is the average over the values of pK_1^0 at each ionic strength. The best value $r = 5.57$ A yields $\overline{pK_1^0} =$

(14) G. Kortüm, "Kolorimetrie, Photometrie und Spektrometrie," 4th ed, Springer-Verlag, Berlin, 1962, p 31.
(15) A. A. Maryott and E. R. Smith, National Bureau of Standards Circular 514, U. S. Government Printing Office, Washington, D. C., 1951.
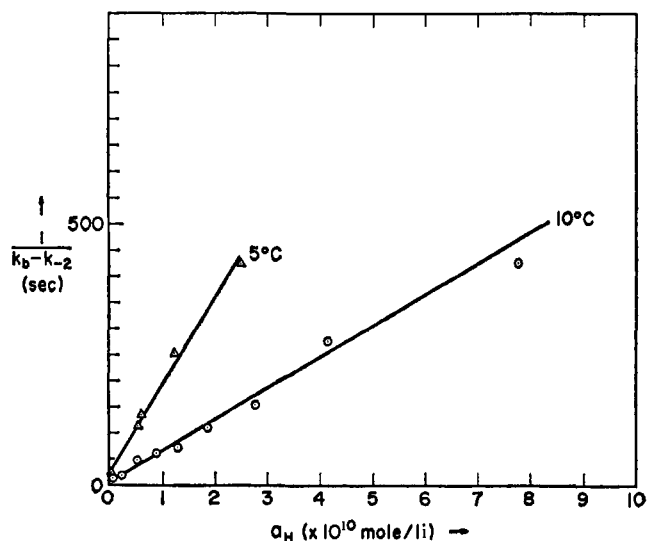
Figure 7. The dependence of $(k_b - k_{-2})^{-1}$ on the hydrogen ion concentration in basic solution at two temperatures.

Figure 8. Arrhenius plot for the rate constant k_{ox} for oxidation of AH', as obtained by optical and epr measurements in acidic solution.

0.15. The same value of r used in conjunction with the data (Table VI) for higher temperatures yielded $\overline{pK_1^0} = 0.07$ (15°), -0.02 (20°), and -0.05 (25°) Fitting to evaluate r was only done at 10° since it proved particularly difficult to measure pK_1 at low ionic strengths at higher temperatures, because low ionic strength limits the extent of pH variation, while the higher temperature caused some side reactions. The above dependence of $\overline{pK_1^0}$ on temperature gave the thermochemical data for the acid dissociation process of BH' as $\Delta H = 5.5 \pm 0.5$ kcal/mole and $\Delta S = 18 \pm 2$ eu. Thus the enthalpy change is close to the typical $O \cdots H$ hydrogen-bond value.

E. Reactions in Alkaline Solutions. If AH' → BH' → B' were the only path for the change from AH' to B', then the rate constant in alkaline solutions should always be equal to k_{-2}, just as in neutral solutions as discussed in section VI-A. In the actual case, however, the reaction rate increases rapidly with hydroxide ion concentration in alkaline solutions. Moreover, $\bar{\epsilon}_0$ at the start of the reaction in this case is not equal to that of AH' but changes with pH and is much greater (3000 at 435 mμ) in strongly alkaline solutions. These facts suggest existence of the fourth ionic species A'. Thus if a reaction scheme with ion A' is assumed as in Table I, the pseudo-first-order rate constant k_b in alkaline solutions at constant pH should be given by eq 6b in section IV, or, expressed in terms of a_H and $K_3 = f_H k_3/k_{-3}$

$$\frac{1}{k_b - k_{-2}} = \frac{1}{k_4 - k_{-2}} + \frac{a_H}{(k_4 - k_{-2})K_3} \qquad (6b')$$

Figure 7 shows that the plots of $(k_b - k_{-2})$ vs. a_H actually give nearly straight lines over the pH range of $\sim 9-11$ as studied at 435 mμ in the 0.1 M NH$_4$OH + 0.1 M NaNO$_3$-0.1 M NH$_4$NO$_3$ aqueous system with ionic strength of 0.1. However, although the slopes of the plot do give the quantity $(k_4 - k_{-2})^{-1}K_3^{-1}$ ($= 1.7 \times 10^{12}$ at 5°, 0.59×10^{12} sec at 10°), the intercepts are too small to yield $k_4 - k_{-2}$ or k_4 itself with a practicable accuracy. Thus, in order to obtain values of the intercept, it proved necessary to measure k_b in strongly alkaline solutions, e.g., in the 0.1 N
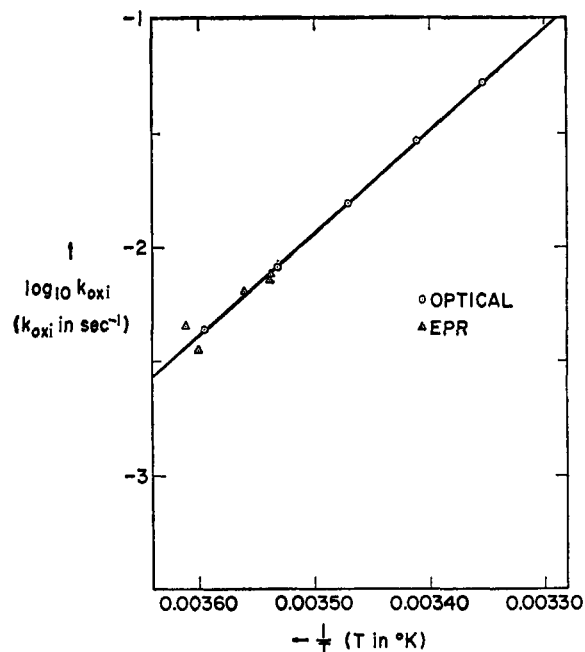
NaOH-0.1 N NaNO$_3$ system with pH as large as 12.9. However, the high rate of the reaction in this region made precise measurements difficult. From the data thus far obtained we could estimate: $k_4 \sim 0.05$ at 5° and ~ 0.1 at 10°. By combining these with the data of $(k_4 - k_{-2})^{-1}K_3^{-1}$ above, we could estimate: $pK_3 \sim 11.0$ at 5° and ~ 10.8 at 10°.
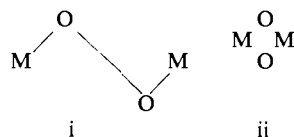
VII. Oxidation Rate of AH' as Studied by Optical and Epr Spectroscopy. The rate of oxidation of AH' to the green paramagnetic ion C' (cf. sections II and III), as measured from the increase of absorbance at 687 mμ (Figure 1), has been found to be independent of the concentration of the acid and the oxidant, provided that both of these are sufficient in quantity for complete oxidation. The rate constant in this case agreed with the rate constant k_{-2} for the conversion reaction AH' → BH' within the experimental error over the temperature range which was examined, 5–25°, as shown in Tables III and IV. In one experiment, in which there was a 50% molar excess of cobalt complex over ceric ion, the reaction proceeded with the same rate constant until the oxidant was exhausted.

The rate of increase of the epr signal after AH' nitrate was dissolved in an acidic Ce(IV) solution also gave a first-order exponential curve, and the rate constants thus obtained fell close to the Arrhenius plot worked out from the optical study (Figure 8). This proves that the rate determined by the optical measurement is actually the rate of the appearance of the paramagnetic ion. Some scattering of the epr data is probably due to the difficulty of controlling the temperature while pouring the reaction mixture into the capillary which was used for epr measurement, especially when the mixture was considerably colder than room temperature.

The above results indicate that whereas BH' or B' is oxidized instantaneously to the paramagnetic ion, AH' is changed to the paramagnetic form only through BH',

the conversion AH′ → BH′ being the rate-determining step. This seems to imply further that BH′ and B′ are structurally more closely related to the paramagnetic form than AH′ is. It was not, however, possible to decide which of BH′ and B′ (or both) is directly oxidized, as their mutual equilibrium is established too quickly.

VIII. On the Nature of the Isomerism of the Diamagnetic μ-Amido-μ-peroxo–Dicobalt Complexes. Two modes by which the peroxo group can coordinate to the

$$
\begin{array}{cc}
\text{i} & \text{ii}
\end{array}
$$

metal ions M appear probable. One is of the σ-bonding type i and the other of the π-bonding type ii. Examples of the latter type have been confirmed in a series of mononuclear peroxo–chromium complexes.[16] X-Ray structural work by Vannerberg on the μ-peroxo-bis(pentaamminecobalt)(4+) ion has disclosed (with reliability index $R = 0.16$) that the peroxo bridge here is of the type σ.[17] As to the structure of the corresponding paramagnetic 5+ ion, Vannerberg and Brosset reported[18] (with $R = 0.20$) that the peroxo bridge in the pentanitrate lies perpendicular to the Co–Co direction (*i.e.*, type π), as suggested by a molecular orbital model of Vlček.[19] However, recent work by Schaefer and Marsh on $[(NH_3)_5CoO_2Co(NH_3)_5]^{5+}$-$SO_4 \cdot (HSO_4)_3$ has disclosed (with $R = 0.077$) that here the peroxo bridge is of type σ.[20] Further, as yet unpublished work by the same authors on the pentanitrate shows that the earlier investigation was indeed in error and that here also the bridge is of the σ type. From the symmetry (C_{2h}) and bond parameters of the 5+ ion (Co–O–O–Co, with bonding as in i, is a molecular symmetry plane; O–O = 1.31 A, ∠Co–O–O = 118°, Co–O = 1.89 A),[20] it seems clear that each oxygen has a well-defined lone pair in the cobalt–oxygen plane xy, and the O–O bond distance suggests that in first approximation the orbital of the unpaired electron is similar to that of O_2^-. The best molecular orbital for the unpaired electron is thus to be formed from the p_z orbitals of the oxygen atoms mixing as an antibonding mixture (π_g^*) with each other and as bonding mixtures with the d_{zz} orbitals of the two cobalt atoms ($x \| Co–O$). It is likely that this orbital is antibonding, so that loss of an electron in going from the 4+ to the 5+ ion is favored in energy; this is consistent with the greater stability of the latter. The unique stability of the cobalt–peroxo system may be explainable in terms of accidental degeneracy of the energy of the d_{zz} cobalt 3+ ion orbital and the π_g^* orbital of O_2^-.

No X-ray structural investigations of any μ-amido-μ-peroxo–dicobalt complexes have yet been reported. However, it seems probable from single crystal epr

studies[21] of the $[(en)_2Co(O_2)(NH_2)Co(en)_2]^{4+}$ ion (C′), dispersed in a $[(en)_2Co(NO_2)(NH_2)Co(en)_2](NO_3)_4$ matrix, that here the peroxo bridge is also of type σ, with the five-atom bridge either planar or with the O_2 group tilted out of the CoNCo plane. It has been found herein (section VII) that ions B′ and BH′ are structurally more closely related to C′ than are ions A′ and AH′, and hence it seems most likely that B′ and BH′ have type σ bridges.

The present research also disclosed that although B′ does not undergo any spontaneous change in water, addition of a proton to B′ induces the transition BH′ → AH′. The energy of activation of this reaction $[(E_{act})_2 = 15.9 \text{ kcal/mole}]$ and that of the reverse one $[(E_{act})_{-2} = 20.7 \text{ kcal/mole}]$ are both of the magnitude required for replacement of a coordinate linkage, so that AH′ must have a structure chemically different from that of BH′, the energy of the former being 5 kcal/mole lower than that of the latter.

It is, of course, difficult to discuss the nature of the isomerism observed in this research in view of the sparse structural information. The fact that no isomerism has been observed in dicobalt complexes with only amido and/or hydroxyl bridges suggests that the peroxo bridge is necessary. However, we have found no evidence from optical absorption studies for existence of isomeric forms of the monobridged μ-peroxo ion in the brown neutral or the red acidic form, or the green paramagnetic form. It has not yet been proved that these three ions all have the same cobalt–peroxo configuration, and it could well be that the second form in each case is too unstable to be appreciable. Thus presence of the second (amido) bridge may be influential in making both isomers stable.

The location of the hydrogen ion in the acidic compounds is, of course, also in need of elucidation. It is clear from the occurrence of the red acidic monobridged peroxo complexes that the proton does occur on the peroxo linkage, rather than involving the amido bridge; this is, of course, more reasonable also from all standard chemical considerations. On the σ-type peroxo bridge, one possible position of H+ is in the oxygen π-electron system normal to the CoO_2Co plane of the monobridged complex, with both atoms left equivalent; the other possible location is at the lone pair of the sp^2 system of either oxygen atom, conceivable with relatively slow proton transfer between the two oxygen sites. Similar considerations hold for the μ-amido-μ-peroxo complexes, although the cobalt and oxygen atoms may well not be perfectly coplanar here, so that the corresponding orbitals are not as clearly defined. In the π-type complex, the most likely position for H+ is in the sp oxygen orbital collinear with the O–O bond, since it does not seem possible for three atoms, *i.e.*, two cobalt and one hydrogen atoms, to be bound in the π system of O_2. In this case the O–H bond is considered to be as strong as the normal O–H bond.

It seems possible that ions B′ and BH′ differ from A′ and AH′ merely by rotation of the oxygen bridge, representing respectively the σ- and π-type complexes. This assumption is in harmony with the magnitude of

(16) E. H. McLaren and L. Helmholz, *J. Phys. Chem.*, **63**, 1279 (1959); R. Stomberg and C. Brosset, *Acta Chem. Scand.*, **14**, 441 (1960); R. Stomberg, *ibid.*, **17**, 563 (1963); *Arkiv Kemi*, **22**, 49 (1964); **23**, 401 (1965); *Nature*, **201**, 486 (1964); **205**, 71 (1965).
(17) N. G. Vannerberg, *Acta Cryst.*, **18**, 449 (1965).
(18) N. G. Vannerberg and C. Brosset, *ibid.*, **16**, 247 (1963); see also C. Brosset and N. G. Vannerberg, *Nature*, **190**, 714 (1961).
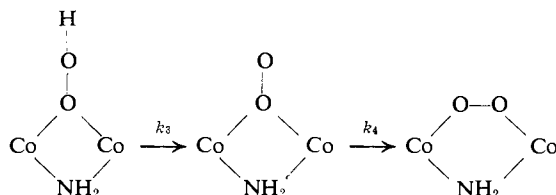(19) A. A. Vlcek, *Trans. Faraday Soc.*, **56**, 1137 (1960).
(20) W. P. Schaefer and R. E. Marsh, *J. Am. Chem. Soc.*, **88**, 178 (1966); *Acta Cryst.*, **21**, 735 (1966).

(21) J. A. Weil, G. L. Goodman, and H. G. Hecht, "Proceedings of the First International Conference on Paramagnetic Resonance, Jerusalem, 1962," Academic Press, Ltd., Jerusalem, 1963, p 880; see also *Bull. Am. Phys. Soc.*, [2] **6**, 152 (1961).

pK_1 ($\sim$0) and pK_3 ($\sim$11), provided the preceding discussion of the bonding of the proton to the peroxo bridge is valid. In this possibility, the fairly large entropy change for the reaction $BH' \rightleftharpoons AH'$ ($\Delta S^{\neq}_2 - \Delta S^{\neq}_{-2} = -16$ eu) presumably requires considering the differences in solvation of the two ions besides the greater flexibility of the σ-type ion, BH'.

It is not possible to dismiss another possibility for the acidic form AH', namely one containing tricovalent oxygen, similar to that reported in a chromium complex.[22] This possibility would also account for the very low value of the acid dissociation constant of AH' ($K_3 \sim 10^{-11}$) comparable to that of H_2O_2 (10^{-12}), as well as for the formation of the σ-type complex after acid dissociation.

Here the complex A' (center) could also be of the π type, for the change from the "tricovalent oxygen" type to the π type does not seem to require much energy and is expected to proceed very rapidly. In the above model for AH', however, the O–O stretching absorption in the neighborhood of 900 cm^{-1} should be infrared active, but was not observable in our studies. Since AH' can be isolated in relatively stable salts, it will be possible to determine its configuration from X-ray structural studies.[22a]

Experimental Section

I. μ-Amido-μ-peroxo-bis{bis(ethylenediamine)cobalt}(4+) Nitrate. This compound was prepared by Werner's method[2a] from μ-amido-μ-peroxo-bis(tetraamminecobalt)(4+) nitrate by applying slightly milder conditions (digestion with en at 60° for 90 min, followed by the treatment with nitric acid at room temperature).

The starting dibridged ammine complex was prepared by a new method of the present authors. It is a result of the study of amido-bridge formation altering the monobridged peroxo–dicobalt–ammine to the dibridged one, and will be shortly communicated as a part of paper II of this series.

II. μ-Amido-μ-peroxo-bis{bis(ethylenediamine)cobalt}(3+) Nitrate-2.5-Water. To a mixture of 3 g of μ-amido-μ-peroxo-bis{bis(ethylenediamine)cobalt}(4+) nitrate (preparation I) and 10 ml of water was added 10 ml of 15 M aqueous ammonia. Acetone (150 ml) was then added little by little while the mixture was stirred. The precipitate was filtered, washed with acetone, and dissolved in a mixture of 10 ml of water and 10 ml of 15 M aqueous ammonia, and the solution was filtered. The complex salt was crystallized out by the slow addition of 150 ml of acetone and cooling, and washed with acetone, yield 1.4 g.

Anal. Calcd for [(en)$_2$Co(NH$_2$)(O$_2$)Co(en)$_2$](NO$_3$)$_3$·2.5H$_2$O: Co, 18.49; C, 15.08; N, 26.37; H, 6.17. Found: Co, 18.81; C, 14.78; N, 26.38; H, 6.31.

III. a. μ-Amido-μ-hydroperoxo-bis{bis(ethylenediamine)cobalt}-(4+) Tetranitrate Dihydrate. This compound was prepared by Thompson and Wilmarth's modification[4] of Werner's method.[2a] Titration with NaOH gave an equivalent weight of 713.7 (expected formula weight of the dihydrate, 691.35). Some contamination with the oxidized form was detected by epr.

b. μ-Amido-μ-hydroperoxo-bis{bis(ethylenediamine)cobalt}(4+) Tetrabromide Monohydrate and μ-Amido-μ-hydroperoxo-bis{bis-

(ethylenediamine)cobalt}(4+) Tetrabromide (Anhydrous). To a solution of 1 g of μ-amido-μ-peroxo-bis{bis(ethylenediamine)cobalt}(3+) trinitrate 2.5-hydrate (preparation II) in 10 ml of water cooled with ice were added an ice-cold mixture of 2.5 ml of 48% hydrobromic acid and 2.5 ml of water, and then 5 g of ammonium bromide. The mixture, cooled in an ice bath, was occasionally stirred and filtered after 30 min. The precipitate was separated and dissolved in 10 ml of a 1:10 mixture of 15 M ammonia and water and cooled with ice, and a mixture of 2.5 ml of 48% hydrobromic acid and 2.5 ml of water was added to it. The mixture was cooled in an ice bath for 30 min, and the precipitate was filtered and washed with ice-cold water containing 2–3% of hydrobromic acid, then with ethanol and ether.

The monohydrate thus prepared was heated at 57° *in vacuo*, until constancy in weight was attained, to obtain red anhydrous bromide. The latter compound showed the same characteristic of conversion $AH' \rightarrow BH'$ when dissolved in water, both qualitatively and quantitatively.

Anal. Calcd for [(en)$_2$Co(NH$_2$)(O$_2$H)Co(en)$_2$]Br$_4$·H$_2$O: Co, 15.82; N, 16.92; Br, 42.91; H$_2$O, 2.42. Found: Co, 15.62; N, 16.79; Br, 42.62; loss *in vacuo*, 2.48. Calcd for [(en)$_2$Co(NH$_2$)-(O$_2$H)Co(en)$_2$]Br$_4$: Co, 16.24; N, 17.37; Br, 44.03. Found: Co, 16.16, 16.39; N, 17.45; Br, 43.93.

IV. μ-Hydroperoxo-bis(pentaamminecobalt)(5+) Trihydrogen Tetrasulfate. First, the corresponding neutral salt, μ-peroxo-bis-pentaamminecobalt)(4+) sulfate dihydrate, was prepared by Fremy's[23] method, namely by the aeration of a *cold* solution of cobalt(II) sulfate in aqueous ammonia.

Five grams of this brown compound was added little by little into 50 ml of ice-cold 3 M sulfuric acid. The dark-colored lumps were ground well with a glass rod until the entire precipitate appeared red and homogeneous. The mixture was then filtered, and the red crystalline precipitate was washed first with cold 3 M sulfuric acid and then once with acetone and next with a 1:1 mixture of acetone and petroleum ether. After a short period of strong suction, the precipitate powder was spread in a Petri dish and quickly placed in a vacuum desiccator, yield 5 g.

Anal. Calcd for [(NH$_3$)$_5$CoO$_2$HCo(NH$_3$)$_5$]H$_3$(SO$_4$)$_4$: Co, 16.64; N, 19.77; S, 18.10. Found: Co, 16.87; N, 19.70; S, 18.14.

There seems to be little doubt that this compound has the same cation as the reddish compound which Vortmann obtained by an analogous procedure[9] and to which he gave the formula

$$Co_2(NH_3)_{10} \left\{ \begin{array}{c} OH \\ OOH \end{array} \right\} (HSO_4)_4$$
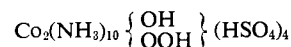
The difference by one molecule of water may have come from the different mode of drying; Vortmann dried his compound over sulfuric acid, while the present authors kept the sample over anhydrous calcium sulfate in an evacuated desiccator.

Optical and Epr Spectra, Kinetic Study, and pK Determination. Optical absorbances of aqueous solutions were recorded with a Cary spectrophotometer, Model 14, both in the static and kinetic studies. The specific diffuse reflectance R_d of powdered samples diluted in potassium sulfate powder was measured in reference to magnesium oxide powder using a Beckman DU spectrophotometer with an integration sphere attachment. The potassium sulfate powder used as the diluent showed a specific diffuse reflectance ranging from 0.98 to 1.01 in reference to magnesium oxide in the region studied.

In the rate study the change of absorbance was followed by the recording device. Special care was necessary for the temperature control in the rate study because the rate was comparatively fast. Thus a calibrated thermometer with scales of 0.1° (readable to 0.01°), which itself had been kept at the desired temperature, was directly immersed in the cell equipped with the circulating system, for the sensitivity of the sensing thermocouple was not sufficient in most cases.

Especially precise temperature control was attained in the rate study $AH' \rightarrow BH'$ because data were not accepted unless the temperature reading showed the desired value to within 0.01° both before and after the rate measurement (including dissolution of AH' nitrate). It was found that the dissolution of a small quantity of sample (1 mg in 3 ml) did not bring about any appreciable temperature change.

Fortunately the crystals of the AH' nitrate dissolved almost instantaneously so that the error caused by the time of solution could be neglected. This was not true, however, with B' nitrate: al-

(22) B. N. Figgis and G. B. Robertson, *Nature*, **205**, 694 (1965).
(22a) NOTE ADDED IN PROOF. Preliminary results, communicated privately by U. Thewalt and R. E. Marsh, disclose that this "tricovalent oxygen" model is indeed the correct one for AH'.

(23) E. Fremy, *Ann. Chim. Phys.*, (3) **25**, 257 (1852); cf. *Chem. Zentr.*, **161**, 185 (1853).

though its solubility is very high, the crystals have a tendency to stick to one another, forming flocks when in contact with water, and this makes the dissolution comparatively slow. In the rate study of B′ ⇌ BH′ → AH′, therefore, a stock solution containing a known amount of B′ was prepared and stored ice-cold, and a certain amount of this stock solution, after being brought to the desired temperature, was mixed with a certain amount of a solution containing perchloric acid and sodium perchlorate. Because of this manipulation the temperature control was not as satisfactory as in the study of AH′ → BH′ or AH′ → C′.

The pH was measured by a Beckman Model G pH meter calibrated by using Beckman standard buffer solutions of pH 4.00 and 6.86.

The epr measurements were carried out with a Varian V-4500 spectrometer with 100-kc/sec modulation, operating at 9500-Mc/sec and room temperature. In contradistinction to any of the other paramagnetic compounds of cobalt, the binuclear cobalt–peroxo complexes show strong epr absorption even at room temperature.

Fitting of straight lines to the experimental points was done with the aid of a least-squares computer program (IBM 1620).

Cyclobutadiene–Metal Complexes. IX.[1]
Tetraphenylcyclobutadienecobalt(I) Complexes[2]

**A. Efraty and P. M. Maitlis**[3]

Contribution from the Department of Chemistry, McMaster University, Hamilton, Ontario, Canada. Received February 28, 1967

Abstract: The complexes $R_4C_4Co(CO)_2X$ (R = C_6H_5, p-$CH_3C_6H_4$; X = halogen) have been prepared by ligand-transfer reactions from $[R_4C_4PdX_2]_2$. The reactions of $R_4C_4Co(CO)_2X$ show considerable similarity to those of π-$C_5H_5Fe(CO)_2X$, and evidence for a very strong metal–ring bond in the cobalt complex is presented. Reaction of $R_4C_4Co(CO)_2Br$ with C_6F_5Li gave the very stable σ-pentafluorophenyl complex $R_4C_4Co(CO)_2C_6F_5$. With aromatic hydrocarbons in the presence of $AlCl_3$, $R_4C_4Co(CO)_2Br$ gave the stable $[R_4C_4Co(arene)]^+$; cycloheptatriene also reacted with $R_4C_4Co(CO)_2Br$ in the absence of a catalyst to give $[R_4C_4CoC_7H_8]^+$. Nucleophilic attack occurred readily at the C_7H_8 ring in $[R_4C_4CoC_7H_8]^+$ and less easily at the benzene ring in $[R_4C_4CoC_6H_6]^+$ to give the $(R_4C_4)Co$(cyclo-heptadienyl) and the $(R_4C_4)Co$(cyclohexadienyl) complexes, respectively. The order of susceptibility of π-complexed ligands in metal d^8 complexes toward nucleophilic attack, cycloheptatriene > benzene > (R_4C_4) > cyclopentadienyl, is proposed. A novel method for effecting hydride abstraction is reported. Aniline in $[Ph_4C_4Co(aniline)]^+$ is less basic than aniline itself by approximately 1.5 pK units.

A general method for the preparation of tetraphenyl-cyclobutadiene (Ph₄C₄) metal complexes by ligand transfer from the readily accessible (Ph₄C₄)–palladium halide complexes[4] (**1a**) has been developed.[5] In these reactions the palladium complex (**1a**) is allowed to react with a metal carbonyl, and transfer of the (Ph₄C₄) group, frequently in high yield, onto the other metal occurs. No detailed studies have yet been carried out on these reactions but a possible mechanism has been outlined.[6] A particularly interesting and fruitful application of this reaction has been to the synthesis of the (tetraphenyl-cyclobutadiene)cobalt dicarbonyl halides (**2a**) by reaction of **1a** with dicobalt octacarbonyl in dichloromethane at 25°.

Results

The complexes **2a** (X = Cl, Br, and I) were obtained from the (Ph₄C₄)–palladium halide complexes **1a** (X = Cl, Br, and I) in yields ranging from 65 to 17% (Table I). The analogous tetrakis(p-tolyl)cyclobutadieneco-balt dicarbonyl bromide (**2b**, X = Br) was obtained

la, R = phenyl
b, R = p-tolyl

2a, R = phenyl
b, R = p-tolyl
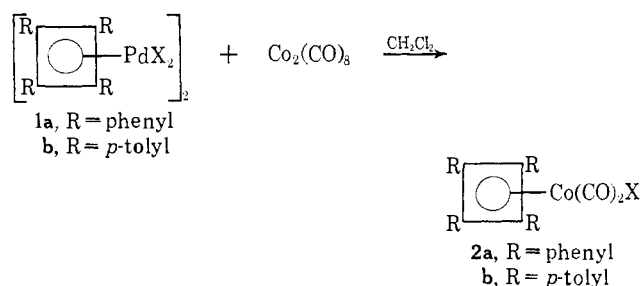
similarly. As obtained, the complexes **2** were usually analytically pure but, as they showed quite a high paramagnetism, it was at first thought that they represented a new type of paramagnetic Co(I) complex.[2a] After very careful purification, however, it has now been possible to obtain this material with quite low magnetic susceptibilities. Solutions of the complexes also show

(1) Part VIII: D. F. Pollock and P. M. Maitlis, *Can. J. Chem.*, **44**, 2673 (1966).

(2) Part of the work described here has been the subject of preliminary communications: (a) P. M. Maitlis and A. Efraty, *J. Organometal. Chem.* (Amsterdam), **4**, 175 (1965); and (b) A. Efraty and P. M. Maitlis, *Tetrahedron Letters*, 4025 (1966).

(3) Author to whom any correspondence should be addressed.

(4) A. T. Blomquist and P. M. Maitlis, *J. Am. Chem. Soc.*, **84**, 2329 (1962); P. M. Maitlis and M. L. Games, *Can. J. Chem.*, **42**, 183 (1964).

(5) P. M. Maitlis and M. L. Games, *J. Am. Chem. Soc.*, **85**, 1887 (1963); *Chem. Ind.* (London), 1624 (1963); P. M. Maitlis and A. Efraty, *J. Organometal. Chem.* (Amsterdam), **4**, 172 (1965).

(6) P. M. Maitlis, *Advan. Organometal. Chem.*, **4**, 109 (1966).