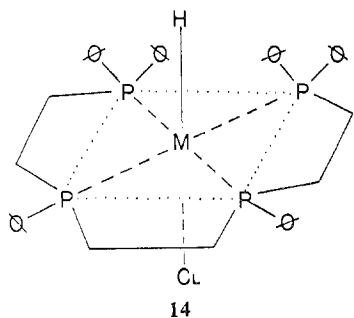The reaction of [Ir(tetraphos-1)]Cl with hydrogen chloride, however, resulted in the formation of *trans*-[Ir(tetraphos-1)-(H)(Cl)]Cl (see **14**) with a metal hydride stretching frequen-

14

cy at 1930 cm^{-1}. The formation of stable hydrides by the oxidative addition reaction of iridium(I) complexes with hydrochloric acid is quite well known.[19,20] Iridium(III) hydrido complexes in general are more stable than the corresponding rhodium(III) complexes.

Oxidative addition of methyl iodide to [M(triphos)(CO)]Cl, [M(tetraphos-1)]Cl, and [M(tetraphos-2)(CO)]Cl resulted in the formation of methyl iodide adducts. Oxidative addition of cationic rhodium complexes of the type [RhL$_4$]$^+$ (L = P-(C$_6$H$_5$)(CH$_3$)$_2$, P(OCH$_3$)$_3$) with methyl iodide was reported by Haines.[21] The adducts obtained in the present investigation were methyl iodide adducts and not the diiodides, as verified by the elemental analysis (Table II). The metal–CH$_3$ peak in the 400–500 cm^{-1} region could not be identified in

(19) J. Chatt, N. P. Johnson, and B. L. Shaw, *J. Chem. Soc.,* 1625 (1964).

(20) J. Chatt, N. P. Johnson, and B. L. Shaw, *J. Chem. Soc. A,* 604 (1962).

(21) L. M. Haines, *Inorg. Chem.,* 10, 1971 (1971).

the ir because of the overlap with the ligational peaks of the polyphosphines. The broad multiplet in the range τ 7.0–8.5 in the nmr spectra of complexes 7–12 of Table IV may be due to the coupling of the coordinated methyl group with the phosphorus atoms in the plane of the metal ion and the methylene groups in a complicated splitting pattern. There was, however, no change in the nmr spectrum of the phenyl protons of the methyl iodide adducts as compared to the original complexes.

As mentioned in the earlier part of the Discussion, iridium(I) and rhodium(I) complexes of poly(tertiary phosphines) form labile adducts with molecular hydrogen and oxygen and as such are possible catalysts in homogeneous hydrogenation and oxygenation reactions. Investigations of catalytic properties of the metal complexes described in this paper are in progress.

Mixed-Ligand Complexes of Terpyridinecobalt(II). New Low-pH Oxygen Carriers[1]

D. H. HUCHITAL[2] and A. E. MARTELL*

Two new mixed-ligand oxygen-carrying cobalt(II) species are reported, Co(terpy)(LL)$^{2+}$, where terpy is terpyridine and LL is 1,10-phenanthroline or 2,2′-bipyridine. These complexes are unique in that they combine with oxygen reversibly in strongly acid solutions, the oxygen uptake being essentially complete at pH 3.0. Equilibrium constants for these oxygen complexes were calculated from both kinetic and potentiometric data. These complexes are also unique in the second-order dependence of the rate of formation of [Co(terpy)(LL)]$_2$O$_2$ on the concentration of Co(terpy)(LL)$^{2+}$. Agreement between kinetic and potentiometric determination of equilibrium constants, second-order dependence on the mixed-ligand complex for oxygen uptake, and the esr of the corresponding superoxide all support a binuclear structure for the oxygen complex.

Introduction

Of the many transition metal complexes that have the ability to absorb oxygen,[3] perhaps the most outstanding are those of cobalt(II).[4] Over the past decade there has been

a resurgence in the study of cobalt(II) complexes, and many studies related to oxygen absorption on the structure, composition, kinetics, and equilibria of these species have been reported.[5-8] The most widely studied, because of their

(1) This work was supported by a research grant, No. GP-33266X, from the National Science Foundation.

(2) Visiting Professor, Texas A&M University, 1972–1973.

(3) For reviews in this area see L. Vaska, *Accounts Chem. Res.,* 1, 335 (1968); J. P. Collman, *ibid.,* 1, 136 (1968); H. Taube, *J. Gen. Physiol.,* 49, 29 (1965).

(4) R. G. Wilkins, *Advan. Chem. Ser.,* **No.** 100 (1971); L. H. Vogt, H. M. Faigenbaum, and S. E. Wiberley, *Chem. Rev.,* 63, 269 (1963).

(5) (a) R. Nakon and A. E. Martell, *Inorg. Chem.,* 11, 1002 (1972); (b) *J. Inorg. Nucl. Chem.,* 34, 1365 (1972); (c) *J. Amer. Chem. Soc.,* 94, 3026 (1972).

(6) F. Miller and R. G. Wilkins, *J. Amer. Chem. Soc.,* 92, 2687 (1970).

(7) M. S. Michailidis and R. B. Martin, *J. Amer. Chem. Soc.,* 91, 4683 (1969).

(8) F. Miller, J. Simplicio, and R. G. Wilkins, *J. Amer. Chem. Soc.,* 91, 1962 (1969).

applicability to biochemical systems, have been the cobalt-(II) complexes with polyamines,[5b,5c,6,8] amino acids,[7,8] and dipeptide ligands.[7] For most of these complexes, the oxygen adduct forms only in basic media. The cobalt(II)–oxygen complexes with triethylenetetramine[5c,6] and tetraethylenepentamine[5b] begin to form at around pH 4 with complete formation at pH 7–8.

We wish to report here two new mixed-ligand cobalt(II) complexes which form oxygen adducts at very low pH. These are the first mixed-ligand cobalt(II) complexes that were found to absorb oxygen with the oxygen uptake being essentially complete at pH 3. The complexes are Co(terpy)-(LL)$^{2+}$ (terpy = 2,2′,2″-terpyridine; LL = 1,10-phenanthroline or 2,2′-bipyridine).

Experimental Section

Materials. The ligands 1,10-phenanthroline hydrochloride and 2,2′-bipyridine hydrochloride were checked for purity by titration with standard KOH solution and were found to be better than 99% pure. Cobalt(II) terpyridine chloride was prepared as described in the literature.[9] All other chemicals used were of reagent grade quality. Standard solutions were prepared by weight in all cases except KOH which was prepared using a commercially available volumetric standard solution.

Apparatus. Potentiometric measurements were taken on a Beckman Research Model pH meter. The hydrogen ion concentration was determined at 25.0 ± 0.05° as previously described.[5a] Kinetic measurements were carried out on a Durrum stopped-flow apparatus. The stopped-flow system was modified to allow for the anaerobic introduction of deaerated solutions. Spectral data were obtained on a Cary Model 14 spectrophotometer. The esr spectrum reported was obtained on a Varian E6S epr spectrometer.

Solution Preparation and Experimental Procedure. Solutions for potentiometric, spectral, or stopped-flow measurements were prepared at ionic strength $I = 0.100$ using potassium nitrate. The hydrogen ion concentration was adjusted using either standard hydrochloric acid or potassium hydroxide as needed. The solutions for the kinetic and spectral runs were purged with argon for 30 min prior to being used.

For the potentiometric experiments, $T = 25°$, the following solutions were measured for $-\log$ [H$^+$] *vs.* KOH added. Set I (under argon): (a) [phenH$^+$] = 1.01 × 10^{-3} M; (b) [Co(terpy)$^{2+}$] = [phenH$^+$] = 1.01 × 10^{-3} M; (c) [Co(terpy)$^{2+}$] = [phenH$^+$] = 1.00 × 10^{-3} M; [added HCl] = 1.00 × 10^{-2} M. Set II (under argon): (a) [bipyH$^+$] = 1.00 × 10^{-3} M; (b) [Co(terpy)$^{2+}$] = [bipyH$^+$] = 1.00 × 10^{-3} M; (c) [Co(terpy)$^{2+}$] = [bipyH$^+$] = 1.00 × 10^{-3} M; [added HCl] = 3.00 × 10^{-3} M. Set III (under oxygen): the above solutions (b) and (c) of sets I and II were repeated under a saturated blanket of oxygen.

Equilibrium data for the interaction of Co(terpy)$^{2+}$ with the protonated ligands (LLH$^+$) were readily obtained from the change in acidity upon complexation using simple charge and material balance equations. Data on the uptake of oxygen by the mixed-ligand complexes were obtained in a similar fashion.

Stopped-flow experiments were followed at 390 nm in the standard way.[10,11] The formation of the oxygen complex was studied by mixing deaerated solutions of terpyridinecobalt(II) (0.8–6.0 mM) with an air-saturated solution containing the bidentate ligand at [H$_3$O$^+$] = 2.4 × 10^{-3} M. Under the conditions used to study the kinetics of O$_2$ uptake the formation reactions (eq 1) have half-lives ≤7.5 msec.

Solutions for esr measurements were prepared by bubbling chlorine gas through a 0.010 M solution of the oxygen adduct [Co(terpy)-(phen)]$_2$O$_2$$^{4+}$ at pH 2.2.
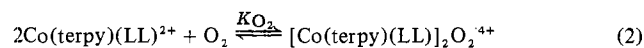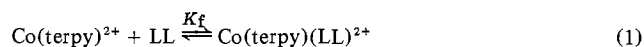
Results and Discussion

Spectral Features. The visible spectra of the mixed-ligand complex Co(terpy)(phen)(OH$_2$)$^{2+}$, its oxygen adduct, and the bis(terpyridine)cobalt(II) chelate, Co(terpy)$_2$$^{2+}$, are reported

(9) R. Hogg and R. G. Wilkins, *J. Chem. Soc.*, 341 (1962).

(10) R. Holyer, C. D. Hubbard, S. F. A. Kettle, and R. G. Wilkins, *Inorg. Chem.*, **5**, 622 (1966).

(11) A value of k_f for the bipyridine system of *ca.* 2 × 10^5 M^{-1} sec^{-1} would lead to log K_f (kinetic) of *ca.* 5.2, which is closer to the potentiometric value.

Table I. Spectral Properties

Complex	λ_{max}, nm	ϵ, M^{-1} cm^{-1}
[Co(terpy)(phen)]$_2$O$_2$$^{2+}$	470 sh	6,150
	390 sh	10,100
Co(terpy)(phen)(OH$_2$)$^{2+}$	548	316
	503	795
	444	1,005
	315	~20,000
Co(terpy)$_2$$^{2+}$	545	550
	505	1,420
	445	1,620

in Table I. As seen from the table, the spectral features of Co(terpy)(phen)$^{2+}$ resemble those of Co(terpy)$_2$$^{2+}$ except for the intensities. Spectral features for the bipyridine complex, not shown, mimic those of the phenanthroline. Thus, an exact spectral analysis could not be undertaken.

Potentiometric and Kinetic Analyses. The results of our potentiometric and kinetic analyses of the equilibria involved in this study are presented in Table II. Calculated values are reported for K_f and K_{O_2}, the equilibrium constants for eq 1 and 2, and the forward and reverse rate constants
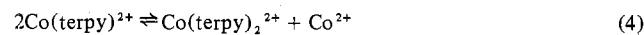
$$\text{Co(terpy)}^{2+} + \text{LL} \xrightleftharpoons{K_f} \text{Co(terpy)(LL)}^{2+} \tag{1}$$

$$2\text{Co(terpy)(LL)}^{2+} + \text{O}_2 \xrightleftharpoons{K_{O_2}} [\text{Co(terpy)(LL)}]_2\text{O}_2{}^{4+} \tag{2}$$

k_f and k_d, where $K_f = k_f/k_d$. Also reported are equilibrium constants K_{fH^+} for reaction 3. The values of K_{fH^+}, k_f, and

$$\text{Co(terpy)}^{2+} + (\text{LL})\text{H}^+ \xrightleftharpoons{K_{fH^+}} \text{Co(terpy)(LL)}^{2+} + \text{H}^+ \tag{3}$$

k_d were useful in the calculations of the kinetic equilibrium constants for eq 2.

Co(terpy)Cl$_2$. The terpyridinecobalt(II) cation cannot be prepared in solution by mixing hexaaquocobaltous ion and free terpyridine. Even very low terpyridine to Co^{2+} ratios result in the exclusive formation of the bis(terpyridine)cobalt(II) complex with the equilibrium shown by eq 4 pre-

$$2\text{Co(terpy)}^{2+} \rightleftharpoons \text{Co(terpy)}_2{}^{2+} + \text{Co}^{2+} \tag{4}$$

dominating to the right. Thus, the terpyridinecobalt(II) complex was isolated as the solid chloride salt. When placed in solution this complex undergoes a slow disproportionation ($t_{1/2} = 2$ hr at 25°), the rate being catalyzed by acid. At [H$_3$O$^+$] = 10^{-3} M, the half-life for reaction 4 drops to approximately 10 min. To avoid errors due to the formation of free Co^{2+} and its subsequent reaction with the bidentate ligands, the solid Co(terpy)Cl$_2$ complex was always added last to the system in the potentiometric experiments. For the stopped-flow experiments, the solid Co(terpy)Cl$_2$ was added as late as possible before each run was initiated.

Under the conditions employed in this study, terpyridinecobalt(II) does not interact with oxygen. At higher $-\log$ [H$^+$] values (>9) the solutions do become darker with the formation of a precipitate. This is probably due to a hydroxide ion catalyzed pathway for the disproportionation reaction 4.

Formation of Mixed-Ligand Complexes. 1,10-Phenanthroline. The log K_f value obtained for eq 1 was 6.55 ± 0.04 (four runs). The value of the potentiometric equilibrium constant K_f is corroborated by stopped-flow determination of the rate constants for the formation and dissociation of the Co(terpy)(phen)$^{2+}$ complex. The values for k_f and k_d are reported in Table II. The value for k_d was obtained by mixing the already formed Co(terpy)(phen)$^{2+}$ complex with excess terpyridine. The rate constant was independent

Table II. Kinetic and Equilibrium Results for the $Co(terpy)^{2+}$-LL-O_2 System

System	Parameter	LL	
		phen	bipy
$Co(terpy)(LL)^{2+}$	log K_f (potentiometric)^a	6.53	5.38
	$10^{-5}k_f, M^{-1}$ sec^{-1}	2.3 ± 0.1	24.8 ± 0.8
	k_d, sec^{-1}	0.063 ± 0.006	1.26 ± 0.10
	log K_f (kinetic)	6.56	6.30
	log K_{fH^+} (av)	1.5	0.98^b
$[Co(terpy)(LL)]_2O_2^{2+}$	log K_{O_2} (potentiometric)	6.85	7.13
	log K_{O_2} (kinetic)^c	6.23	6.30

^{a} Error limits on log K values are ±0.04 to ±0.07. ^{b} Potentiometric data only. ^{c} See text and Table III.

Table III. Kinetic Data on the Formation of Oxygen Adducts

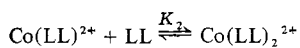| Ligand (LL)	$10^4[Co(terpy)LL^{2+}], M$	$10^4[O_2], M$	k_{obsd}, sec^{-1}	$10^{-5}k_{3rd},^b M^{-1}$ sec^{-1}
1,10-Phenanthroline	4.0	1.3	0.161^a	10.1
	7.0	1.3	0.385^a	7.85
	12.0	1.3	1.100	7.64
	30.0	1.3	7.37	8.19
	2.0	2.0	c	8.52^d
				Av 8.46 ± 0.68
2,2'-Bipyridine	12.0	1.3	1.41	9.8

^{a} Data for first 50% of reaction. ^{b} $k_{3rd} = k_{obsd}/[Co(terpy)(LL)]^2$. ^{c} Half-life = 44 sec. ^{d} $k_{3rd} = 3/(2t_{1/2}A_0^2)$.

of the concentration of excess terpyridine added. The value of log K_f obtained from kinetic data is 6.56, in excellent agreement with the potentiometric results.

2,2'-Bipyridine. The agreement between kinetic and potentiometric equilibrium constants K_f is slightly poorer when LL is 2,2'-bipyridine. The potentiometric value of log K_f obtained for the formation of $Co(terpy)(bipy)^{2+}$ was 5.38 ± 0.06. The value of log K_f obtained from kinetic data is 6.30. The reasons for the discrepancy are not known.

The formation rate constants, k_f, reported here do not seem to reflect the enhanced reactivity of $Co(terpy)^{2+}$ observed with terdentate ligands.[10] It would seem that bidentate substitution on $Co(terpy)^{2+}$ differs from terdentate substitution. Furthermore, the larger k_f value for bipyridine compared to that for phenanthroline cannot be explained.[11] Data on similar systems are lacking and studies into this area are being pursued.

It is interesting to note that log K_f values obtained in this study compare very reasonably with the second formation constants for the reaction

$$Co(LL)^{2+} + LL \xrightleftharpoons{K_2} Co(LL)_2^{2+}$$

In the case of 1,10-phenanthroline log K_2 is 6.70[12] while log K_f for eq 1 is 6.55. Likewise, for LL = 2,2'-bipyridine log K_2 is 5.60[12] as compared with log K_f = 5.38 the potentiometric value for this study.
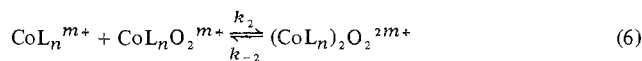
Formation of Oxygen Adducts. At $-\log[H^+] = 3$ under argon the extent of formation of the mixed-ligand complexes is >80%. This strong binding is reflected in a large drop in pH when the second ligand hydrochloride is added to the $Co(terpy)^{2+}$ solution. Addition of oxygen at this point further increases the concentration of H_3O^+ in solution. However, under these conditions this increase is too small to be useful in equilibrium calculations. Therefore, the formation constant K_{O_2} corresponding to eq 2 was calculated at $-\log[H^+] = 2.000$ for 1,10-phenanthroline and at $-\log[H^+] = 2.520$ for 2,2'-bipyridine. The values of K_{O_2} obtained are 7.06×10^{-6} and $1.34 \times 10^7 M^{-2}$ for the 1,10-phenanthroline and 2,2'-bipyridine complexes, respectively (log values listed in Table II).

(12) J. Simplicio and R. G. Wilkins, *J. Amer. Chem. Soc.*, **89**, 6092 (1967).

Data on the kinetics of the formation of the oxygen complexes are presented in Table III. The rate of formation was found to be second order in $[Co(terpy)(LL)^{2+}]$ (LL = 1,10-phenanthroline) and first order in $[O_2]$ under our experimental conditions. The third-order rate constant, obtained by dividing the observed first-order rate constant by $[Co(terpy)(phen)^{2+}]^2$, is $(8.45 ± 0.83) \times 10^5 M^{-2}$ sec^{-1}. The second-order dependence on $[Co(terpy)(phen)^{2+}]$ and the overall third-order dependence were checked in a kinetic run performed at equal concentrations of both mixed-ligand complex and oxygen $(2.0 \times 10^{-4} M)$. For a third-order reaction at equal concentrations, the rate constant is given by $k = 3/(2t_{1/2}A_0^2)$. The half-life was 44 sec yielding $k = 8.5 \times 10^5 M^{-2}$ sec^{-1} in agreement with the value obtained above.

With LL = 2,2'-bipyridine only one stopped-flow run was performed. The third-order rate constant obtained was $9.8 \times 10^5 M^{-2}$ sec^{-1}.

Although the order of reaction observed in this system differs from the order observed by Wilkins for the formation of other oxygen complexes, our second-order dependence supports the overall mechanism proposed by Wilkins.[4] According to this scheme, the formation of the oxygen adduct is considered to take place *via* a two-step process, *viz.*

$$CoL_n^{m+} + O_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CoL_nO_2^{m+} \tag{5}$$

$$CoL_n^{m+} + CoL_nO_2^{m+} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} (CoL_n)_2O_2^{2m+} \tag{6}$$

Assuming steady-state conditions the initial rate is given by (7). Under conditions of a moderate to large excess of

$$\frac{d[(CoL_n)_2O_2^{2m+}]}{dt} = \frac{k_1k_2[CoL_n^{m+}]^2[O_2]}{k_{-1} + k_2[CoL_n^{m+}]} \tag{7}$$

CoL_n^{m+} the rate of formation of the oxygen adduct becomes pseudo first order $(=k_{obsd}[O_2])$. Individual rate constants (k_1) or ratios of rate constants (k_{-1}/k_1k_2) have been obtained by Wilkins and coworkers in systems involving polyamines, histidine, and histamine.[6,8,11] In the latter two cases as well as that of diethylenetriamine neither term in the denominator of eq 7 is dominant and rate data were obtained by plotting $[CoL_n^{m+}]/k_{obsd}$ *vs.* $[CoL_n^{m+}]^{-1}$. Except for one set of data taken at 4°, only values of k_1 could be
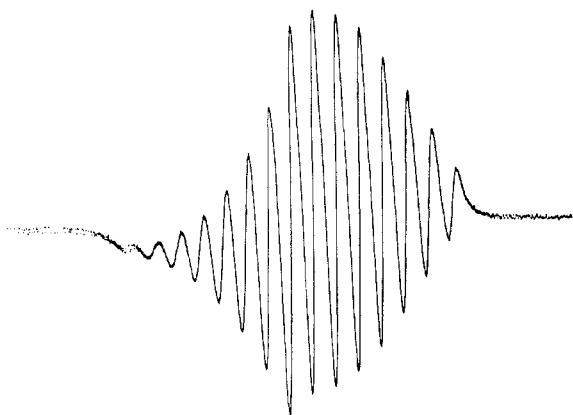
Figure 1. Esr spectrum of $[Co(terpy)(phen)]_2O_2^{3+}$, 0.01 M, pH 2.2.

accurately reported.[12] For other polyamines[8] $k_2 [CoL_n^{m+}] \gg k_{-1}$ and eq 7 reduced to a simple second-order rate expression with r_{obsd} $(M^{-1}$ sec$^{-1}) = K_1 [CoL_n^{m+}][O_2]$.

In our systems, the second-order dependence on the concentration of the mixed-ligand complex is the first example of the limiting case where $k_{-1} \gg k_2 [CoL_n^{m+}]$. The third-order rate constant obtained (column 4 in Table III) is thus $k_1 k_2 / k_{-1}$. A value of k_{-2} was obtained by reaction of the equilibrated system under oxygen with dithionite ion. Under conditions of [oxygen adduct] = 5 $\times$ 10^{-4} M and of varying $S_2O_4^{2-}$ concentration, the loss of the brown color associated with the oxygen adduct (λ 490 nm) is first order with $k_{-2} = 0.50 \pm 0.04$ sec^{-1} for LL = phen and bipy. With values of $k_1 k_2 / k_{-1}$ and k_{-2} a direct comparison with the potentiometric equilibrium constants was made. The results are reported in Table II. While the potentiometric and kinetic K_{O_2} values are not identical, they are quite close and within the range expected for comparisons of this type based on kinetic and potentiometric data.

Esr. In conjunction with similar experiments being carried out in these laboratories on bridged μ-peroxo-cobalt(III) species, an esr spectrum of the green product obtained on Cl$_2$ oxidation of $[Co(terpy)(phen)]_2O_2^{4+}$ was taken. The spectrum (Figure 1) shows 15 lines with peak separations of ca. 10 G. This is indicative of a binuclear superoxo complex with the free electron residing on the dioxygen linkage (Figure 2).

Conclusions

Agreement between kinetic and potentiometric equilibria analyses, the second-order dependence on [Co(terpy)-(phen)]$^{2+}$ for the O$_2$ uptake, and the esr of the superoxo complex all support the assignment of a binuclear structure
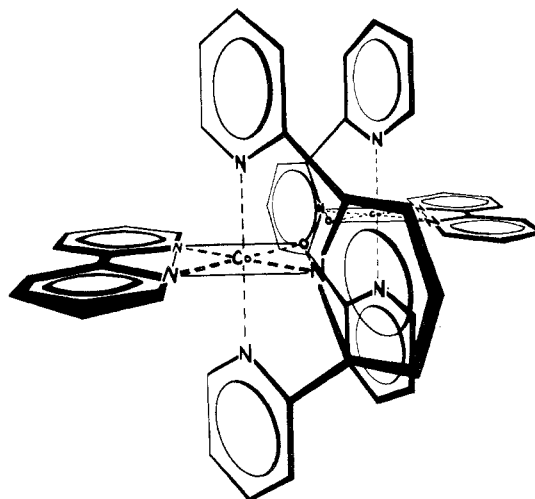

Figure 2. Proposed structure of $[Co(terpy)(phen)]_2O_2^{3+}$ obtained on Cl$_2$ oxidation of the binuclear $[Co(terpy)(phen)]_2O_2^{2+}$.

to the oxygen adduct.[13] The adduct however is not stable to reversibility experiments. Continued deaeration and aeration of the solution with argon and oxygen, respectively, eventually lead to a yellow solution of what seems to be the cobalt(III) species which can no longer absorb oxygen.

Initial studies on the decomposition of the oxygen adduct showed a half-life for decomposition of approximately 2 hr at pH 3 and 88 min at pH 4. At this latter pH an experiment was performed in the presence of 0.005 M Fe^{2+} (adduct concentration 8.5 $\times$ 10^{-5} M). The half-life for the formation of the red iron–immine complex was 75 min. This strongly indicates that the decomposition of the oxygen adduct may involve the loss of a phenanthroline ligand. Further work on this aspect is being carried out.

The mixed-ligand system described in this paper affords an excellent opportunity to observe the effects of the ligand LL on the oxygen uptake. We are currently exploring other bidentate ligands with oxygen and sulfur as well as with nitrogen donors.

(13) Solid samples of the mixed-ligand complex under argon and oxygen atmospheres were obtained by precipitation as the hexafluorophosphate salts. The results were 9.04% N for [Co(terpy)-(phen)(OH$_2$)](PF$_6$)$_4$ compared to a calculated value of 8.97 and 8.96% N for [Co(terpy)(phen)]$_2$O$_2$(PF$_6$)$_4$ compared to a calculated value of 9.00. The 1:1 oxygen adduct [Co(terpy)(phen)O$_2$](PF$_6$)$_2$ would require 8.82% N. Although these values are quite close, they supply additional evidence of a 2:1 metal:oxygen stoichiometry.