Inorg. Chem. **1994,** *33,* 2841–2847

Cobalt(II) Polypyridine Complexes and Their Reversible Reactivity with Dioxygen

Dorai Ramprasad, Andrew G. Gilicinski, Thomas J. Markley, and Guido P. Pez[*]

Corporate Research Group, Air Products and Chemicals, Inc., Allentown, Pennsylvania 18195-1501

Received August 4, 1993[•]

The synthesis and characterization of cobalt(II) polypyridine complexes of general formula [Co(terpy)(B)X]X is described, where terpy = 2,2′:6′,2″-terpyridine, B = 2,2′-bipyridine (bpy), 1,10-phenanthroline, or various ring-substituted phenanthrolines, and X^- is a weakly binding ligand or counteranion. The complexes react reversibly with dioxygen in polar nonaqueous solvents forming 2:1 Co to O_2 adducts, which exist as μ-peroxo dimers. The structure of $[[Co(terpy)(bpy)]_2(\mu\text{-}O_2)](PF_6)_4{\cdot}2CH_3COCH_3$ (**2a**) was determined by single-crystal X-ray crystallography: crystal space group $P\bar{1}$ with $a = 10.953(2)$ Å, $b = 12.509(3)$ Å, $c = 14.426(3)$ Å, $\alpha = 105.15(2)°$, $\beta = 103.41(2)°$, and $\gamma = 110.39(2)°$. In the cation of **2a** the O–O distance for the bridging peroxo ligand (1.419(7) Å) is at the short end of the usual range (1.41–1.49 Å). Formation constants for the Co(II) polypyridine complexes' O_2 adducts were determined electrochemically and were found to be dependent on the donor properties of the ligand B, the anion X, and on the solvent. In nitrobenzene solution, these dioxygenation constants are significantly reduced by the addition of X = triflate and X = 4-chloro-3-nitrobenzenesulfonate ligands which compete for the O_2-coordination site. The presence of a coordinated triflate in $[Co(terpy)(3,4,7,8\text{-tetramethyl-1,10-phenanthroline})CF_3SO_3]CF_3SO_3$ (**7**) was demonstrated by single-crystal X-ray crystallography: for $C_{33}H_{27}CoF_6N_5O_6S_2$ (**7**) space group $P2_1/c$, with $a = 8.827(2)$ Å, $b = 20.815(5)$ Å, $c = 19.121(6)$ Å, $\beta = 98.80(2)°$, and $Z = 4$. Intensity data were taken on a Nicolet R3m diffractometer in the range of $4° \leq 2\theta \leq 50°$. A total of 6525 (6135 independent) reflections were collected; of these 3769 had $F_o > 5\sigma(F_o)$. The structure was solved by direct methods and refined to $R(F) = 5.13\%$ and $R_w(F) = 5.40\%$. Hydrogen atom contributions with $D(\text{C–H}) = 0.96$ Å were included. Further details are given in Tables 3 and 4 and in the supplementary material. The cation (Figure 2) consists of a Co(II) ion coordinated by molecules of tetramethyl-1,10-phenanthroline (bidentate) and terpyridine (tridentate) and an O-bound triflate ion for which $D(\text{Co–O}) = 2.165(3)$ Å. The various synthesized Co(II) polypyridine complexes are relatively long-lived reversible dioxygen carriers. Solutions of $[[Co(terpy)(4,7\text{-diphenyl-1,10-phenanthroline})]_2(\mu\text{-}O_2)](triflate)_4$ (**5**) (0.1 M) under O_2 were found to retain 60% of their O_2 activity after 60 days at 25 °C (a projected half-life of 8 months). A method was found for partially regenerating the spent dioxygen carriers. Heating the spent oxygen carrier solutions under N_2 to 150 °C followed by cooling in air resulted in their partial regeneration to O_2-active species.

Introduction

The reversible binding of dioxygen to various classes of transition metal complexes has been extensively studied and is the subject of several excellent reviews.[1,2] Much of the impetus for this work has come from a desire to prepare O_2-coordination complexes which model the natural dioxygen carriers, hemoglobin, myoglobin, hemocyanin, etc. Dioxygen complexes have also played an important role in the field of metal-catalyzed oxidation chemistry; there has also been a continuing interest in their potential use in air separation and dioxygen-removal processes.[3] A major barrier to this has been the limited operational lifetime of all known metal–O_2 carriers (including the biological systems). Invariably, the reversible O_2-binding properties are lost, usually by a combination of metal ion and ligand oxidation reactions.[4] Since the latter processes are essentially irreversible, we sought to prepare O_2 carriers utilizing relatively oxidatively "robust" ligands.

We describe here the synthesis and structure of several cobalt(II) polypyridine-ligand complexes of general formula [Co(terpy)(B)X]X, where terpy = 2,2′:6′,2″-terpyridine, B = 2,2′-bipyridine (bpy), 1,10-phenanthroline, or various ring-substituted 1,10-phenanthrolines, and X is a weakly binding anionic ligand or counteranion such as triflate. The complexes' reversible dioxygen-binding properties in nonaqueous media were demonstrated and quantified from a combination of electrochemical, UV/vis, IR, and Raman spectral data. Some of the O_2 adducts were found to be reasonably long-lived in nonaqueous solvents, with observed half-lives of up to 8 months at room temperature. Also, a simple method was found for partially regenerating complexes that had lost dioxygen binding activity over time.

Experimental Section

General Methods. Infrared spectra were obtained with a Nicolet 510 FTIR spectrometer. UV/vis spectra were recorded with a Beckman DU-70 spectrophotometer. Raman spectra were obtained with an ISA-3000 instrument using a 514-nm laser source. Elemental analyses were done in-house or at Oneida Research Services (Whitesboro, NY 13492).

Metal Complex Synthesis. The starting complexes $Co(terpy)Cl_2$ and $Co(terpy)Br_2$ were prepared by literature methods.[5] 2,2′-Bipyridine, 1,10-phenanthroline, and the other polypyridine ligands were obtained from Aldrich and used as received. The solid dioxygen complexes were handled in air without any special precautions.

Preparation of $[Co(terpy)(bpy)]_2O_2(PF_6)_4$ (2). A mixture of $Co(terpy)Br_2$ (0.4 g, 0.89 mmol), 2,2′-bipyridine (0.15 g, 0.96 mmol), and NH_4PF_6 (0.35 g, 2.1 mmol) in methanol (100 mL) was stirred for 10 min under ambient air. The resulting brown precipitate was filtered off and washed with methanol (20 mL) and diethyl ether. It was then dissolved in a minimum volume of acetone and reprecipitated by the addition of ether. More acetone was added to this mixture until it became deep red in color. The remaining brown solid (0.33 g, 50%) was isolated by

---

[*] Author to whom correspondence should be addressed.

[•] Abstract published in *Advance ACS Abstracts,* April 1, 1994.

(1) Jones, R. D.; Summerville, D. A.; Basolo, F. *Chem. Rev.* **1989,** *79,* 139.

(2) Niederhoffer, E. C.; Timmons, J. H.; Martell, A. E. *Chem. Rev.* **1984,** *84,* 137.

(3) Norman, J. A. T.; Pez, G. P.; Roberts, D. A. Reversible Complexes for the Recovery of Dioxygen. In *Oxygen Complexes and Oxygen Activation by Transition Metals*; Martell, A. E., Sawyer, D. T., Eds.; Plenum Press: New York, 1988.

(4) (a) Shikama, K. *Coord. Chem. Rev.* **1988,** *83,* 73. (b) Chen, D.; Martell, A. E.; Sun, Y. *Inorg. Chem.* **1989,** *28,* 2647. (c) Bush, D. H. Synthetic Dioxygen Carriers for Dioxygen Transport. In *Oxygen Complexes and Oxygen Activation by Transition Metals*; Martell, A. E., Sawyer, D. T., Eds.; Plenum Press: New York, 1988.

(5) Harris, C. M.; Lockyer, T. N.; Martin, R. L.; Patil, H. R. H.; Sinn, E.; Stewart, I. M. *Aust. J. Chem.* **1969,** *22,* 2105.

0020-1669/94/1333-2841$04.50/0

filtration, washed with ether, and dried at 100 °C under vacuum for 1 h. Anal. Calcd for $C_{50}H_{38}N_{10}Co_2O_2P_4F_{24}\cdot H_2O$: C, 39.30; H, 2.62; N, 9.17. Found: C, 39.12; H, 2.69; N, 9.06.

Preparation of $[Co(terpy)(bpy)](PF_6)_2$ (1). Solutions of **1** were prepared by purging **2** in CH_3CN with N_2 until the redox wave at $E_{1/2} = 0.837$ V (vs Ag/0.01 M $AgNO_3$ reference) disappeared.

Preparation of $[Co(terpy)(bpy)]_2O_2(CF_3SO_3)_4$ (3). To the complex **2** (0.10 g, 0.07 mmol) in 20 mL of acetone was added tetrabutylammonium triflate (0.50 g, 1.28 mmol) (under ambient air). The solution was stirred for 10 min, and then the solvent was removed under vacuum giving a dark oily residue. Trituration of this residue in the presence of added methylene chloride resulted in the precipitation of a brown solid, which after filtration was redissolved in a minimum volume of acetone. More tetrabutylammonium triflate (0.5 g) was added, and the solvent was removed under vacuum. Addition of methylene chloride led to the precipitation of the desired product (0.065 g, 65%). Anal. Calcd for $C_{54}H_{38}N_{10}Co_2O_{14}S_4F_{12}\cdot 2H_2O$: C, 41.51; H, 2.49; N, 8.97. Found: C, 41.33; H, 2.61; N, 8.82.

Preparation of $[[Co(terpy)(B)]_2O_2](CF_3SO_3)_4$ Complexes. Complexes with B = 1,10-phenanthroline (**4**), 4,7-diphenyl-1,10-phenanthroline (**5**), and 3,4,7,8-tetramethyl-1,10-phenanthroline (**6**) were prepared by the reaction described by eq 4. Typically, to a mixture of $Co(terpy)Cl_2$ (1.1 mmol), $AgOSO_2CF_3$ (2.2 mmol), and B (1.1 mmol) was added 30 mL of acetone and the contents were stirred in air for 1 h while cooling in ice water. The solution was filtered (to remove the AgCl) and the filtrate poured into 250 mL of hexane to yield a dark brown oil. This was dissolved in a minimum quantity of acetone. A solid precipitate formed upon the subsequent addition of ether. The solid was redissolved in acetone, and the solution was set aside to crystallize. The product was washed with ether and dried in vacuum. $[Co(terpy)(1,10\text{-phenanthroline})]O_2(CF_3SO_3)_4\cdot 2H_2O$ (**4**): Yield 45.5%. Anal. Calcd for $C_{58}H_{38}N_{10}Co_2O_{14}S_4F_{12}\cdot 2H_2O$: C, 43.26; H, 2.61; N, 8.70. Found: C, 43.33; H, 2.60; N, 8.66. $[Co(terpy)(4,7\text{-diphenyl-}1,10\text{-phenanthroline})]_2O_2(CF_3SO_3)_4\cdot 2H_2O$ (**5**): Yield 62%. Anal. Calcd for $C_{82}H_{54}N_{10}Co_2O_{14}S_4F_{12}\cdot 2H_2O$: C, 51.47; H, 2.92; N, 7.32. Found: C, 51.42; H, 3.16; N, 6.99. $[Co(terpy)(3,4,7,8\text{-tetramethyl-}1,10\text{-phenanthroline})]_2O_2(CF_3SO_3)_4\cdot 2H_2O$ (**6**): Yield 65%. Anal. Calcd for $C_{66}H_{54}N_{10}F_{12}S_4O_{14}Co_2\cdot 2H_2O$: C, 46.05; H, 3.37; N, 8.14; Co, 6.84. Found: C, 45.82; H, 3.06; N, 8.01, Co, 6.74.

Preparation of $[Co(terpy)(3,4,7,8\text{-tetramethyl-}1,10\text{-phenanthroline})(CF_3SO_3)]CF_3SO_3$ (7). A solution of the O_2 complex **6** (0.070 g) in 3 mL of nitrobenzene was warmed to ~100 °C and then purged with dinitrogen. The resulting dedioxygenated solution was cooled, filtered, and covered with a layer of hexane. On standing (under N_2), a crystalline solid appeared. Its structure was determined by single-crystal X-ray crystallography to be the title complex **7**. In a solution of the crystalline solid the 670-nm absorption which is a characteristic of all the present O_2 complexes was absent, which is consistent with its characterization in the solid state as a cobalt-bound triflate complex (refer to Figure 3).

Complexes with B = 5-chloro-1,10-phenanthroline (**8**) and 5-nitro-1,10-phenanthroline (**9**) were prepared by the reaction described by eq 4, in nitrobenzene. Because of the relatively weak and very labile O_2 binding in these complexes, it was not possible to obtain analytically pure materials. The compounds were only characterized by their electrochemical properties in solution under N_2 and O_2 (see Table 5) and by their UV/vis spectrum (band at 670 nm characteristic of the O_2 adduct). Cyclic voltammetry (CV) data for compounds **1**–**9** recorded under N_2 and O_2 are collected in Table 5.

X-ray Data Collection, Structure Determination, and Refinement[6] for $[[Co(terpy)(bpy)]_2(\mu\text{-}O_2)](PF_6)_4\cdot 2CH_3COCH_3$ (2a). A crystal of approximate dimensions 0.41 × 0.30 × 0.22 mm was grown from a solution of **2** in acetone/pentane. Data were taken on a Nicolet R3m diffractometer in the range of $4° \le 2\theta \le 50°$. A total of 6117 (5860 independent) reflections were collected; of these 3930 had $F_0 > 5\sigma(F_0)$. The structure was solved by direct methods. All computations were done using programs in the SHEL XTL library (version 4.2). Hydrogen atom contributions with D(C–H) = 0.96 Å were included. Further details appear in Table 1.

Electrochemistry. Measurements were made using a BioAnalytical Systems 100A potentiostat. For the cyclic voltammetry studies scan rates of 0.1 V/s were employed. A 3-mm glassy-carbon electrode (BioAnalytical Systems) was used in conjunction with platinum wire as a counter electrode. The reference was Ag/0.010 M $AgNO_3$ in acetonitrile or nitrobenzene and electrolyte (measured in both solvents at +0.292 V vs SCE, saturated calomel electrode). $E_{1/2}$ values were reproducible to ±0.005 V for the dimer complex and ±0.01 V for unbound forms. Solutions (generally 1×10^{-3} M in Co) were prepared in previously dried and distilled acetonitrile or nitrobenzene containing 0.1 M tetrabutylammonium tetrafluoroborate (Southwest Analytical) or triflate (Fluka) salts (used as received).

Table 1. Crystal Data and Summary of Intensity Data Collection and Structure Refinement for $[[Co(terpy)(bpy)]_2(\mu\text{-}O_2)](PF_6)_4\cdot 2CH_3COCH_3$ (**2a**)

formula	$(C_{50}H_{38}N_{10}O_2Co_2)(PF_6)_4\cdot 2C_3H_6O$
fw	1624.65
cryst system	triclinic
space group	$P\bar{1}$
a, Å	10.953(2)
b, Å	12.509(3)
c, Å	14.426(3)
α, deg	105.15(2)
β, deg	103.41(2)
γ, deg	110.39(2)
V, Å^3	1670.6(7)
Z	1
ρ(calcd), g cm^{-3}	1.615
T, K	295
λ, Å	0.710 73
μ(Mo Kα), cm^{-1}	6.97
R, R_w, %[a]	6.78, 7.51
GOF	1.400
$\Delta(\rho)$, e A^{-3}	0.905

[a] $R(F) = \sum(|F_o| - |F_c|)/\sum(|F_o|)$, where F_o and F_c are respectively the observed and calculated structure factors. $R_w(F) = \sum(w^{1/2}(|F_o| - |F_c|))/\sum(w^{1/2}|F_o|)$, where $w^{-1} = \sigma^2(F_o) + g(F_o)^2$ and $g = 0.001$.

Dioxygen Binding Constants. A dioxygen binding constant, log K_{O_2} (M^{-1} atm^{-1}), was defined for the dioxygen binding equilibrium of these complexes in solution according to the 2:1 Co:O_2 stoichiometry of eq 6 (*vide infra*). Cyclic voltammetry data allowed the concentration of both the dioxygenated and undioxygenated metal complex species in the equilibrium to be measured simultaneously at any partial pressure of dioxygen. Peak currents were measured for the redox waves for both species, and concentrations were calculated from these currents using the following equation:[7]

$$i_{\text{peak}}(\text{reversible}) = (2.69 \times 10^5)n^{2/3}AD_0^{1/2}v^{1/2}C_0 \qquad (1)$$

where i is the peak current, n is the number of electrons transferred, A is the electrode area, v is the scan rate, and C_0 and D_0 are the required concentration and the diffusion coefficient, respectively, of the reacting species. Equation 1 applies for conditions of reversible electron transfer kinetics. This was usually the case for the O_2 adducts, as indicated by a 60–80-mV separation of peak potentials. However, peak separations of 100–200 mV were typically seen in redox waves for the undioxygenated complexes. In these cases, the data were treated using a method adapted from the theoretical work of Matsuda and Ayabe.[7,8] The peak current for the quasi-reversible wave is reduced by a factor $K(\Lambda,\alpha)$, where Λ is a function of the rate constant for the electrode reaction and α is the transfer coefficient for the electrode reaction. In this work, α was assumed to be 0.5 and Λ was calculated on the basis of the observed peak separations as described in ref 6. Results were compared to full digital simulations[9] of several voltammograms for $[Co(terpy)(bpy)](PF_6)_2$ (**1**) and were found to be in good agreement as evidenced by a close match of simulated and experimental voltammograms.

The diffusion coefficient, D_0 in eq 1 for each species (both dioxygenated and undioxygenated), was evaluated separately in chronocoulometry experiments. Results were calculated from eq 2, which expresses the

$$Q = (2nFAD_0^{1/2}C_0t^{1/2})/\pi^{1/2} \qquad (2)$$

relationship between charge and time for diffusion-limited current after

---

[6] The X-ray structural work reported in this paper on compounds **2a** and **7** was done by Dr. A. Rheingold, University of Delaware, Newark, DE 19716.

[7] Bard, A. J.; Faulkner, L. R. *Electrochemical Methods: Fundamentals and Applications*; Wiley: New York, 1980.

[8] Matsuda, H.; Ayabe, Y. *Z. Electrochem.* **1955**, *59*, 494.

[9] Simulation program obtained from D. Gosser; see: Gosser, D.; Rieger, P. *Anal. Chem.* **1988**, *60*, 1159.

a potential step.[7] In eq 2 Q is the charge, F is the Faraday constant, t is time, and the other terms are as in eq 1. Typical diffusion coefficients for $[Co(terpy)(bipy)](PF_6)_2$ (**1**) in acetonitrile were 2.0×10^{-5} cm²/s; in nitrobenzene the value for the triflate salt was 1.0×10^{-5} cm²/s, and in γ-butyrolactone it was 1.3×10^{-5} cm²/s. Diffusion coefficients for the dimer species were typically 10–40% lower. In cases of extremely weak or strong O_2 binding, where the fully undioxygenated or dioxygenated species could not be generated, the diffusion coefficient for the unmeasured species was estimated from the most closely related data for other complexes in the same solvent. The number of electrons n for the dimer was taken to be 1; other values gave unreasonably low diffusion coefficients. This is consistent with the peak separations of 60–80 mV that were seen for the reversible dimer couple, instead of the lower values expected for a reversible two-electron wave.

This electrochemical technique afforded K_{O_2} values with a probable error of ±5% with the uncertainties originating from the peak current and peak potential measurements. An additional error of ±5% is expected in cases where measurements on both the undioxygenated and dioxygen-bound species could not be made (vide supra). As a check of the technique, K_{O_2} was determined for $[Co(terpy)(bpy)](PF_6)_2$ (**1**) in CH_3CN and compared with K_{O_2} as determined by conventional spectrophotometric methods[10] utilizing the 670-nm absorption for the O_2 complex **2**. There was good agreement between the two: $\log K_{O_2} = 4.4 \pm 0.2$ (electrochemical, with added 0.1 M $N(Bu)_4PF_6$) versus $\log K_{O_2} = 4.0$ (spectrophotometric, with no added electrolyte).

Heats of reaction were determined from electrochemical data taken at various temperatures. In these experiments, temperature was varied by using a jacketed electrochemical cell and a Lauda Model RC-6 circulating bath to maintain temperature. Solution temperature was monitored with a thermometer in the cell.

Result and Discussion

Synthesis of $[Co(terpy)(bpy)]^{2+}$ and Its Dioxygen Adduct, $[[Co(terpy)(bpy)]_2O_2](PF_6)_4$. In 1973 Huchital and Martell[11a,b] deduced the formation of $[Co(terpy)(bpy)]^{2+}$ and $[Co(terpy)(phen)]^{2+}$ complexes in aqueous solutions[11c] by potentiometric and kinetic analysis methods. At pH 3.0 under air, the former complex formed a 2:1 cobalt to O_2 adduct with a half-life of ca. 2 h at room temperature. Lunsford et al.[13] later reported on the synthesis of a mononuclear reversible O_2 adduct $[Co^{III}(terpy)(bpy)O_2^-]^{2+}$ trapped within the cage of a Y zeolite. Its probable composition was deduced from the method of synthesis and EPR spectra. We aimed to prepare these and related cobalt(II) polypyridine complexes in aprotic media where a greater operational stability (i.e. half-life) of their O_2 adducts might be realized.

In our initial attempts at preparing $[Co(terpy)(bpy)]^{2+}$ salts, $Co(terpy)Cl_2$ was reacted with silver hexafluorophosphate and 2,2′-bipyridyl in acetonitrile, under a dinitrogen atmosphere, as shown in eq 3. Surprisingly, solutions in acetonitrile of the

$$Co(terpy)Cl_2 + 2AgPF_6 + bpy \xrightarrow{N_2} \underset{\mathbf{1}}{[Co(terpy)(bpy)](PF_6)_2} + 2AgCl \ldots \quad (3)$$

expected product **1** were found to be inactive toward dioxygen (by UV/vis measurements). However, the same reaction when conducted in air led to an isolated solid which when redissolved in acetonitrile gave O_2 reversibly reactive solutions. Cyclic voltammetry (CV) scans of these solutions performed under N_2 (Figure 1a) gave two reversible oxidation waves: a major species at $E_{1/2} = -0.04$ V and a minor component at $E_{1/2} = 0.21$ V. When the same CV analyses were done under dioxygen, the magnitude of the major −0.04 V wave remained unchanged, the minor feature at 0.21 V diminished in intensity, and a new oxidation wave appeared at $E_{1/2} = 0.837$ V. The reaction in eq 3 conducted in air had thus afforded a mixture containing, as only a minor component, an O_2-reactive species with a characteristic redox potential of 0.21 V vs Ag/0.01 M $AgNO_3$.

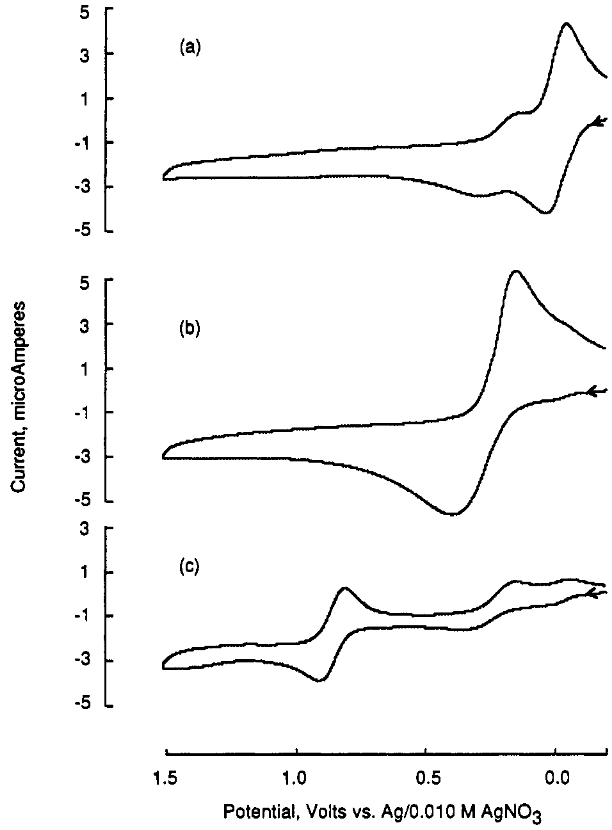

Figure 1. (a) Cyclic voltammogram (CV) of solutions of "crude" $[Co(terpy)(bpy)](PF_6)_2$ in acetonitrile under N_2: only the minor component at $E_{1/2} = 0.21$ V is O_2-reactive. (b) CV of pure O_2-active $[Co(terpy)(bpy)](PF_6)_2$ (**1**) under N_2 ($E_{1/2} = 0.21$ V). (c) CV of O_2-active $[Co(terpy)(bpy)](PF_6)_2$ (**1**) under O_2 showing both the undioxygenated and dioxygenated species, the latter at $E_{1/2} = 0.837$ V. Scan rate = 100 mV/s. All potentials are vs the Ag/0.01 M $AgNO_3$ reference, measured to be +292 mV vs SCE.

Attempts at increasing the yield of this "O_2-active $[Co(terpy)(bipy)]^{2+}$" component led to the synthesis of its μ-peroxo adduct **2** by the reactions shown in eqs 4 and 5. The second procedure

$$2Co(terpy)Cl_2 + 4AgPF_6 + 2bpy \xrightarrow[air]{CH_3COCH_3} \underset{\mathbf{2}}{[[Co(terpy)(bpy)]_2O_2](PF_6)_4} + 4AgCl \ldots \quad (4)$$

$$2Co(terpy)Br_2 + 4NH_4PF_6 + 2bpy \xrightarrow[air]{CH_3OH} \underset{\mathbf{2}}{[[Co(terpy)(bpy)]_2O_2](PF_6)_4} + 4NH_4Cl \ldots \quad (5)$$

is particularly convenient since the O_2 complex product precipitates and can thus be isolated in a state of high purity. This O_2 adduct **2** was characterized by a combination of elemental analyses and an X-ray structural determination (vide infra).

Cyclic voltammetry scans of solutions of **2** of acetonitrile under O_2 (Figure 1c) show a redox wave for the O_2-reactive $[Co(terpy)(bpy)]^{2+}$ species ($E_{1/2} = 0.21$ V) and a characteristic wave for

---

(10) Smith, T. D.; Pilbrow, J. R. *Coord. Chem. Rev.* **1981**, *39*, 295.

(11) (a) Huchital, D. H.; Martell, A. E. *J. Chem. Soc., Chem. Commun.* **1973**, 868. (b) Huchital, D. H.; Martell, A. E. *Inorg. Chem.* **1976**, *15*, 2966. (c) Solid samples of the $[Co(terpy)(phen)]^{2+}$ complex were obtained by precipitation as the hexafluorophosphate salts under Ar and O_2. On the basis of only an analysis for nitrogen, it was suggested that the materials have the composition of $[Co(terpy)(phen)OH_2](PF_6)_4$ and $[Co(terpy)(phen)]_2O_2(PF_6)_4$, respectively.

(12) Johnson, C. K. ORTEP-II, Report ORNL-5138; Oak Ridge National Laboratory: Oak Ridge, TN, 1976.

(13) Imamura, S.; Lunsford, J. H. *Langmuir* **1985**, *1*, 326.

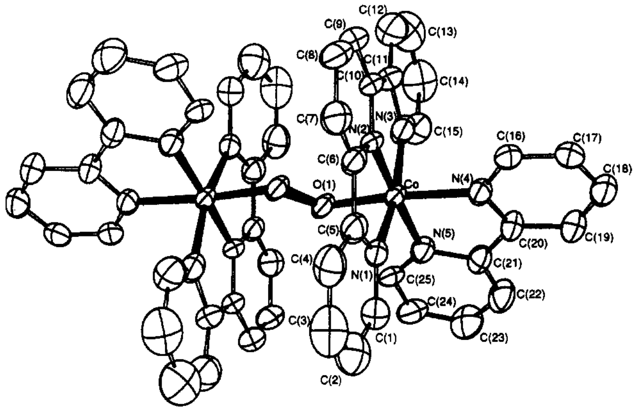

Figure 2. Structure of the μ-peroxo complex (4+) cation in $[[Co(terpy)(bpy)]_2(\mu\text{-}O_2)](PF_6)_4$ (**2**).

its O_2 adduct **2** at $E_{1/2}$ = 0.837 V. On the basis of chronocoulometry measurements (see Experimental Section) this wave is assigned to a one-electron oxidation/reduction of **2** to $[Co(terpy)(bipy)]_2O_2^{5+}$. Huchital et al.[11b] prepared an EPR-characterized cobalt(III) μ-superoxo complex of the related composition $[Co(terpy)(phen)]^{2+}$ by oxidizing an aqueous solution of $[Co(terpy)(phen)]_2O_2^{4+}$ with chlorine.

Purging solutions of $[[Co(terpy)(bpy)]_2O_2](PF_6)_4$ (**2**) in acetonitrile led to the quantitative formation of the initially desired $[Co(terpy)(bpy)](PF_6)_2$ complex **1**, having the characteristic $E_{1/2}$ of 0.21 V (Figure 1b). Significantly, in the CV scan of these solutions of **1**, there is only a small residue of the wave at $E_{1/2}$ = −0.04 V for the O_2-inactive species.

Structure of $[[Co(terpy)(bpy)]_2(\mu\text{-}O_2)](PF_6)_4{\cdot}2CH_3COCH_3$ (2a). Single crystals of the title cobalt(III) μ-peroxo complex **2a** (the acetone solvate of **2**) were grown from acetone/pentane solutions and its structure determined by X-ray diffraction. An ORTEP[12] plot of the complex cation is shown in Figure 2. Its hexafluorophosphate counterion is present as a totally separated entity. Crystal data are summarized in Table 1; positional coordinates for atoms of the cation and selected bond lengths and angles are shown in Tables 2 and 3, respectively.

The metal complex cation has a crystallographically imposed inversion center at the midpoint of the O–O bond. The μ-peroxo bond (1.419(7) Å) is at the short end of the usual range suggesting a considerable $\pi^* \rightarrow d$ orbital back-donation. This finding seems consistent with the complex's observed reversible O_2 binding in solution. The cobalt coordination geometry is distorted octahedral, which is mostly attributable to the chelate ring dimensions determined by the rigid ligand frameworks. The bpy and terpy planes are nearly perpendicular. The two outer terpy Co–N distances are identical, and the inner distances are predictably shorter. The two bpy Co–N distances differ significantly: N(4)–Co = 1.992(3) and N(5)–Co = 1.938 Å. As expected, the longer distance is trans to the O_2 ligand.

In addition to four PF_6^- counterions for each Co_2 complex the lattice contains two molecules of acetone per Co dimer unit. The ions pack freely without significant interionic contacts or contacts to acetone.

Formation and Properties of $[[Co(terpy)(bpy)]_2O_2](PF_6)_4$ (2) in Acetonitrile. Solutions of $[Co(terpy)(bpy)](PF_6)_2$ (**1**) in CH_3CN prepared by purging **2** with N_2 (vide supra) reversibly react with O_2 according to the following stoichiometry:

$$2[Co(terpy)(bpy)]^{2+} + O_2 \rightleftarrows [Co(terpy)(bpy)]_2O_2^{4+} \quad (6)$$

Table 2. Positional Parameters (×10^4) for Significant Atoms in $[[Co(terpy)(bpy)]_2(\mu\text{-}O_2)](PF_6)_4{\cdot}2CH_3COCH_3$ (**2a**)

	x	*y*	*z*
Co	7156.4(7)	6499.5(6)	948.4(5)
O(1)	5434(4)	5131(4)	503(3)
N(1)	7592(4)	5615(4)	−153(3)
N(2)	6553(4)	7119(4)	−10(3)
N(3)	6450(4)	7469(4)	1760(3)
N(4)	9066(4)	7882(4)	1620(3)
N(5)	7889(4)	5920(4)	1970(3)
C(1)	8039(6)	4736(5)	−187(5)
C(2)	8138(7)	4057(7)	−1045(5)
C(3)	7794(8)	4283(7)	−1934(6)
C(4)	7343(6)	5182(6)	−1924(5)
C(5)	7243(5)	5838(5)	−1028(4)
C(6)	6695(5)	6763(5)	−931(4)
C(7)	6298(6)	7240(5)	−1644(4)
C(8)	5711(7)	8053(6)	−1401(5)
C(9)	5532(6)	8373(5)	−468(5)
C(10)	5968(5)	7886(5)	234(4)
C(11)	5899(5)	8099(5)	1269(4)
C(12)	5337(7)	8816(7)	1733(6)
C(13)	5308(8)	8915(7)	2711(7)
C(14)	5853(8)	8277(7)	3196(6)
C(15)	6406(6)	7558(6)	2701(5)
C(16)	9567(6)	8881(5)	1389(4)
C(17)	10874(6)	9801(5)	1943(5)
C(18)	11735(7)	9734(6)	2753(6)
C(19)	11241(6)	8700(6)	2997(5)
C(20)	9877(5)	7772(5)	2414(4)
C(21)	9242(5)	6654(5)	2609(4)
C(22)	9896(6)	6328(6)	3351(4)
C(23)	9150(7)	5231(6)	3443(5)
C(24)	7779(7)	4513(6)	2814(5)
C(25)	7196(6)	4875(5)	2079(4)

Table 3. Selected Bond Lengths and Bond Angles in the Cation of $[[Co(terpy)(bpy)]_2(\mu\text{-}O_2)](PF_6)_4{\cdot}2CH_3COCH_3$ (**2a**)

	Bond Lengths (Å)		
Co–O(1)	1.875(3)	Co–N(3)	1.942(5)
Co–N(1)	1.943(5)	Co–N(4)	1.992(3)
Co–N(2)	1.856(5)	Co–N(5)	1.938(5)
O(1)–O(1a)	1.419(7)	N(1)–C(1)	1.346(9)
C(1)–C(2)	1.357(10)	N(2)–C(6)	1.349(8)
C(24)–C(25)	1.368(11)	N(3)–C(11)	1.382(9)
C(5)–C(6)	1.469(10)	C(20)–C(21)	1.463(9)
	Bond Angles (deg)		
O(1)–Co–N(1)	89.2(2)	O(1)–Co–N(2)	94.5(2)
N(1)–Co–N(2)	82.4(2)	O(1)–Co–N(3)	88.6(2)
N(1)–Co–N(3)	164.9(2)	N(2)–Co–N(3)	82.8(2)
O(1)–Co–N(4)	170.7(2)	N(1)–Co–N(4)	94.1(2)
N(2)–Co–N(4)	94.6(2)	N(3)–Co–N(4)	90.5(2)
O(1)–Co–N(5)	88.7(2)	N(1)–Co–N(5)	97.2(2)
N(2)–Co–N(5)	176.8(2)	Co–O(1)–O(1A)	112.6(4)
N(4)–Co–N(5)	82.2(2)		

The dioxygenation reaction is accompanied by a color change from orange to deep brown which corresponds to the appearance of a characteristic maximum at 670 nm in the visible spectrum. For this absorption, ϵ = 900 M^{-1} cm^{-1} at 0 °C where the complex is almost totally in the dioxygenated form. The formation of this μ-peroxo complex was confirmed by Raman spectral measurements: Upon dioxygenating CH_3CN solutions of **1** a new band appeared at 824 cm^{-1}, which was shifted to 782 cm^{-1} on using $^{18}O_2$. The frequency is typical for the symmetric ν(O–O) stretching vibration of μ-peroxo cobalt complexes: 1:1 cobalt to O_2 "end-bound" or 2:1 cobalt to O_2 μ-superoxo complexes would be expected to show characteristic ν(O–O) stretching vibrations at ca. 1100 cm^{-1}.[13] In our Raman and electrochemical studies of the reaction of **1** with dioxygen, surprisingly, we saw no evidence for the formation in solution at room temperature of the $[Co(terpy)(bipy)O_2]^{2+}$ superoxo complex which Lunsford et al[13] identified as an entrapped species in a zeolite matrix.

Since both **1** and its O_2 complex **2** are seen in the cyclic voltammogram of CH_3CN solutions of **1** under dioxygen, it was possible to determine the formation constant of the O_2 adduct (log K_{O_2}) entirely from electrochemical data. Details of the method are given in the Experimental Section. For the formation of $[[Co(terpy)(bpy)]_2O_2](PF_6)_4$ in CH_3CN, log K_{O_2} = 4.4 (M^{-1} atm^{-1}) at 25 °C (cf. Table 5). This may be compared to the

Table 4. Positional Parameters ($\times 10^4$) for Significant Atoms in [Co(terpy)(3,4,7,8-tetramethyl-1,10-phenanthroline)CF_3SO_3]CF_3SO_3 (7)

	x	*y*	*z*
Co	31.4(7)	2369.9(3)	5143.9(3)
F(1)	−3642(4)	1828(2)	2911(2)
F(2)	−1442(4)	2000(2)	2632(2)
F(3)	−2407(6)	1064(2)	2538(2)
S(1)	−1384(1)	1394(1)	3832(1)
O(1)	−1207(4)	2024(2)	4150(2)
O(2)	38(4)	1097(2)	3747(2)
O(3)	−2451(4)	993(2)	4104(2)
N(1)	1164(4)	2897(2)	6008(2)
N(2)	419(4)	3242(2)	4669(2)
N(3)	2045(4)	1819(2)	5065(2)
N(4)	−331(4)	1528(2)	5645(2)
N(5)	−2067(4)	2538(2)	5547(2)
C(1)	1464(5)	2723(2)	6684(3)
C(2)	2154(5)	3119(2)	7237(2)
C(3)	2567(5)	3737(2)	7074(3)
C(4)	2287(5)	3932(2)	6360(2)
C(5)	1561(5)	3501(2)	5849(2)
C(6)	2690(6)	4546(2)	6104(3)
C(7)	2353(7)	4717(3)	5422(3)
C(8)	1552(6)	4298(2)	4897(3)
C(9)	1188(5)	3685(2)	5120(2)
C(10)	1115(6)	4468(2)	4180(3)
C(11)	352(6)	4019(3)	3725(3)
C(12)	34(5)	3414(2)	3997(3)
C(2A)	2377(6)	2855(3)	7972(3)
C(3A)	3291(7)	4187(3)	7641(3)
C(10A)	1481(7)	5124(3)	3910(3)
C(11A)	−169(7)	4135(3)	2954(3)
C(13)	3224(5)	2006(3)	4761(3)
C(14)	4424(6)	1598(3)	4667(3)
C(15)	4384(6)	982(3)	4911(3)
C(16)	3190(6)	786(3)	5233(3)
C(17)	2024(5)	1207(2)	5299(2)
C(18)	651(5)	1042(2)	5625(2)
C(19)	354(7)	442(3)	5889(3)
C(20)	−989(7)	362(3)	6163(3)
C(21)	−1975(6)	868(3)	6192(3)
C(22)	−1606(5)	1453(2)	5928(2)
C(23)	−2538(5)	2047(2)	5924(2)
C(24)	−3769(5)	2109(3)	6285(3)
C(25)	−4553(6)	2685(3)	6244(3)
C(26)	−4090(6)	3173(3)	5854(3)
C(27)	−2851(6)	3089(3)	5514(3)
C(28)	−2262(7)	1587(3)	2925(3)

literature[11b] value of log $K_{O_2} = 4.23$ (M^{-1} atm^{-1}) for [Co(terpy)(bpy)]$_2O_2^{4+}$ complex in water at pH = 2.52 (estimated from ref 11b using an O_2 solubility in H_2O of 1.26×10^{-3} M atm^{-1}).

While the above dioxygenation reaction of **1** in CH_3CN was entirely reversible over a period of several hours, the solutions lost much of their O_2-binding activity over longer times (ca 7% loss/day). Surprisingly, this degradation occurred under either O_2 or N_2. In cyclic voltammetry studies of **1** in CH_3CN under N_2, the amplitude of the redox wave for **1** at $E_{1/2} = 0.21$ V diminished with time and was accompanied by the growth of the wave at $E_{1/2} = -0.04$ V for the above cited "O_2-inactive [Co(terpy)(bpy)]$^{2+}$" species in acetonitrile. It was concluded that the observed slow deactivation of **1** takes place substantially by a structural rearrangement process rather than metal or ligand oxidation. Either of the latter two processes would have resulted in $E_{1/2}$ values at far more positive potentials.

Synthesis and O_2-Binding Properties of [Co(terpy)(bpy)X](X) Complexes in Nitrobenzene (X = Anionic Ligand or Counteranion). To mitigate this unexpected structural instability of [Co(terpy(bpy)](PF_6)$_2$ (**1**) in acetonitrile, we studied its behavior in other solvents as well as the effect of adding metal-coordinating anions. As a coordinating solvent, acetonitrile could conceivably aid in the rearrangement of the active complex **1** by partially displacing the terpy or bpy ligands. Several other solvents were tried including *N,N*-dimethylformamide, *N*-methylpyrrolidinone, dimethyl sulfoxide, sulfolane, and nitrobenzene. Of these, nitrobenzene, though the least coordinating,[15] still has a relatively high dielectric constant which we found to be a necessary property for solubilizing the complexes. Solutions of [Co(terpy)(bpy)]$_2^{4+}$ (cation of **2**) in nitrobenzene were indeed found to be long-lived. However, the dioxygen was now so tightly bound (log K_{O_2} too high to measure by electrochemistry) that it could not be released by purging with N_2. We now had a very stable dioxygen adduct but at the expense of facile reversibility.

To regain the O_2 reversibility we examined the effect of replacing PF_6^- in **1** with potentially metal-ligating counteranions (X^-). By competing with O_2 for the sixth coordination site of cobalt, the latter ions might be expected to lower the effective dioxygen affinity of [Co(terpy)(bpy)](PF_6)$_2$ (**1**) in nitrobenzene. In a search for suitable counteranions the UV/vis spectra were taken of solutions of [Co(terpy)(bpy)]$_2O_2$(PF_6)$_4$ (**2**) in nitrobenzene to which such species, X^-, were added as tetraalkylammonium salts. The solutions were monitored by changes in the intensity of the ~670-nm band, which is characteristic of the O_2 adduct. Addition of NO_3^-, $CH_3SO_3^-$, and $C_6H_5SO_3^-$ salts resulted in a total loss of O_2 reactivity; these anions are presumably too strongly bound to cobalt. However, using triflate, $CF_3SO_3^-$, and 4-chloro-3-nitrobenzenesulfonate ((CNB)SO_3^-) anions led to solutions having reversible dioxygen binding. This was confirmed by K_{O_2} measurements for solutions of [Co(terpy)(bpy)CF_3SO_3]CF_3SO_3 and [Co(terpy)(bpy)((CNB)SO_3)]((CNB)SO_3) in nitrobenzene, for which log K_{O_2} (M^{-1} atm^{-1}) is 4.8 and 1.5 (at 25 °C), respectively. The O_2 adduct of the former complex (compound **3**) was also obtained as a discrete solid (see Experimental Section). The cited dioxygenation constants may be compared with log K_{O_2} = 4.4 (M^{-1} atm^{-1}) for the O_2-reversibly reactive solutions of [Co(terpy)(bpy)](PF_6)$_2$ (**1**) in acetonitrile. Further support for the notion of lowering O_2 affinity by the use of competing ligands came from the following studies of 1,10-phenanthroline-ligated complexes.

Synthesis and O_2 Reactivity of [Co(terpy)(phen)]X_2 Complexes. The reversibly O_2-reactive solutions of [Co(terpy)(bpy)CF_3SO_3]CF_3SO_3 in nitrobenzene proved to be significantly more stable (longer-lived) than those of [Co(terpy)(bpy)](PF_6)$_2$ (**1**) in acetonitrile. However, to arrive at the best possible systems for long-term stability studies the range of complex compositions was broadened by replacing bpy with ring-substituted phenanthroline (phen) ligands. Typically Co(terpy)Cl_2, silver triflate, and the phen ligand were reacted in acetone or nitrobenzene under ambient air giving the following dioxygenated complexes: [Co(terpy)(phen)]$_2O_2$(CF_3SO_3)$_4$, where phen = 1,10-phenanthroline (**4**), 4,7-diphenyl-1,10-phenanthroline (**5**), 3,4,7,8-tetramethyl-1,10-phenanthroline (**6**), 5-chloro-1,10-phenanthroline (**8**), and 5-nitro-1,10-phenanthroline (**9**) (see Experimental Section).

The formation constant (log K_{O_2}) for the [[Co(terpy)(phen)]$_2O_2$](CF_3SO_3)$_4$ complexes and electrochemical redox ($E_{1/2}$) data for both the dioxygenated and undioxygenated forms are summarized in Table 5. For some of the [[Co(terpy)(B)]$_2O_2$](X)$_4$ complexes (B = bpy, phen; X = CF_3SO_3, 4-chloro-3-nitrobenzenesulfonate ((CNB)SO_3)) log K_{O_2} was determined in various solvents, as a function of temperature. Heats of dioxygenation ($\Delta H°$) were calculated from a plot of K_{O_2} vs $1/T$; these results are also given in Table 5.

The collected log K_{O_2} data exemplify the well-known[14] dependence of O_2-binding constants on the electron density on cobalt. For instance the dioxygenation constant (K_{O_2}) for [Co(terpy)(3,4,7,8-tetramethyl-1,10-phenanthroline)]$_2O_2$(PF_6)$_4$ (**6**) is about 1 order of magnitude greater than for its 1,10-phenanthroline ligand analog **4**. Conversely, by using nitro and chloro substituents on the 1,10-phenanthroline ligand, the dioxygenation constant is markedly reduced. The electrochemical

---

(14) Nakamoto, K. *Coord. Chem. Rev.* **1990**, *100*, 363.

Table 5. Electrochemical Redox Data, Dioxygenation Constants (log K_{O_2}), and Heats of Dioxygenation for $[Co(terpy)B]X_2$ Complexes

O_2 complex, with specified anion	ligand (B)	ligand/ anion X	solvent	$E_{1/2}$[Co(II↔III)] for [Co(terpy)B]X, V[a,e]	$E_{1/2}$ oxidn of $[Co(terpy)B]_2O_2X_4$, V[a,f]	log K_{O_2} at 25 °C, M^{-1} atm^{-1}	$-\Delta H(O_2)$, kcal/mol
2[b]	bpy	PF_6^-	CH_3CN	0.21	0.837	4.4 (22 °C)[h]	
	bpy	$CF_3SO_3^-$	CH_3CN	0.23	0.835	4.7 (22 °C)[h]	
	bpy	PF_6^-	$C_6H_5NO_2$	g	0.895	>6.0[g]	
3	bpy	$CF_3SO_3^-$	$C_6H_5NO_2$	0.33	0.853	4.8[h]	41
	bpy	$(CNB)SO_3^-$ [d]	$C_6H_5NO_2$	0.26	0.848	1.5[i]	30
3	bpy	$CF_3SO_3^-$	γ-butyrolactone	0.17	0.755	2.9 (20 °C)[h]	19
4	1,10-phen[c]	PF_6^-	CH_3CN	0.25	0.852	3.8[h]	
6	3,4,7,8-tetramethyl-1,10-phen[c]	PF_6^-	CH_3CN	0.14	0.767	4.9[h]	
8	5-Cl-1,10-phen[c]	$CF_3SO_3^-$	$C_6H_5NO_2$	0.43	0.911	2.2[i]	39
9	5-NO_2-1,10-phen[c]	$CF_3SO_3^-$	$C_6H_5NO_2$	0.40	0.903	3.0[h]	
5	4,7-diphenyl-1,10-phen[c]	$CF_3SO_3^-$	$C_6H_5NO_2$	0.32	0.817	4.7[h]	
5	4,7-diphenyl-1,10-phen[c]	PF_6^-	CH_3CN	0.19	0.816	4.2[h]	

[a] Versus Ag/0.01 M $AgNO_3$ electrode, in the stated solvent. [b] **1** is the corresponding undioxygenated complex. [c] phen = phenanthroline. [d] 4-Chloro-3-nitrobenzenesulfonate ($(CNB)SO_3^-$). [e] Error in measurements is ±0.01 V. [f] Error in measurements is ±0.005 V. [g] Value could not be measured (undioxygenated complex was below limit of detection). [h] Values have an error of ±5%, from error in peak current values (as discussed in text). [i] Values have an error of ±10%, due to additional uncertainty in diffusion coefficients (see text).

$E_{1/2}$ values for both the complexes and their O_2 adducts vary in parallel with these changes in K_{O_2}. Thus for decreasing values of K_{O_2}, the $E_{1/2}$ waves are generally shifted to more positive potentials consistent with the removal of electron density from cobalt.

The data in Table 5 show how K_{O_2} is also greatly affected by the donor ability of the complex's counteranion ($(CNB)SO_3^- > CF_3SO_3^- > PF_6^-$) and of the solvent[15] (γ-butyrolactone > CH_3CN > $C_6H_5NO_2$). In general, competition for the dioxygen coordination site on cobalt by counteranion or solvent results in lower dioxygen binding constants. There is also a corresponding decrease in the heat of dioxygenation (which is actually the enthalpy change for O_2 replacing a ligand on the coordination site). Thus for the $[Co(terpy)(bpy)]^{2+}$ complex, $-\Delta H(O_2)$ decreases from 41 to 30 kcal/mol by changing the counteranion from triflate to 4-chloro-3-nitrobenzenesulfonate ($(CNB)SO_3^-$). Using γ-butyrolactone as the solvent, the heat is diminished to as low a value as 19 kcal/mol.

Solutions of complexes listed in Table 5 with log K_{O_2} < ca. 4.8 are practically-reversible dioxygen carriers in that the O_2 can be totally liberated by purging with dinitrogen at or slightly above room temperature. It was possible in some cases to isolate the resulting undioxygenated complex from its solutions. The structure of [Co(terpy)(3,4,7,8-tetramethyl-1,10-phenanthroline)(CF_3SO_3)]CF_3SO_3 (**7**) was elucidated by single-crystal X-ray crystallography (Figure 3; Table 4). It was shown to contain one coordinated triflate (D(Co–OSO_2CF_3 = 2.165(3) Å) thus providing support for the results of our solution studies on the effect of added ligands on K_{O_2} (*vide supra*). Further details of the complex's structure are provided in the Abstract and as supplementary material.

Long-Term Stability and Regeneration Studies. The relative stability (operational lifetime) of the dioxygen complexes listed in Table 5 was determined by monitoring changes in their electrochemical properties and UV/visible spectra with time. Initial results led to the identification of [[Co(terpy)(4,7-diphenyl-1,10-phenanthroline)]$_2O_2$]$(CF_3SO_3)_4$ (**5**) as the most promising candidate for longer term studies.

Changes occurring in a 1.33 × 10^{-3} M solution of **5** (a) in nitrobenzene dedioxygenated and kept under rigorously dry N_2 and (b) in nitrobenzene in dry O_2 (1 atm) were followed by periodic electrochemical CV scans over 180 days. Results are shown in the upper two curves of Figure 4. Over this time the sample under dinitrogen decomposed retaining 67% of its original activity, as estimated from the current for the wave at $E_{1/2}$ = 0.32 V. The decomposition product (also in nitrobenzene) gave a redox wave with $E_{1/2}$ = 0.06 V. The O_2-exposed sample, however, retained only 42% of its original activity. Byproducts were an O_2-inactive species (41%) with $E_{1/2}$ = 0.06 V and some Co(III) as evidenced by a small reduction current at the start of the CV scan at −0.2 V. The identification of these decomposition products will require further investigation.[16]

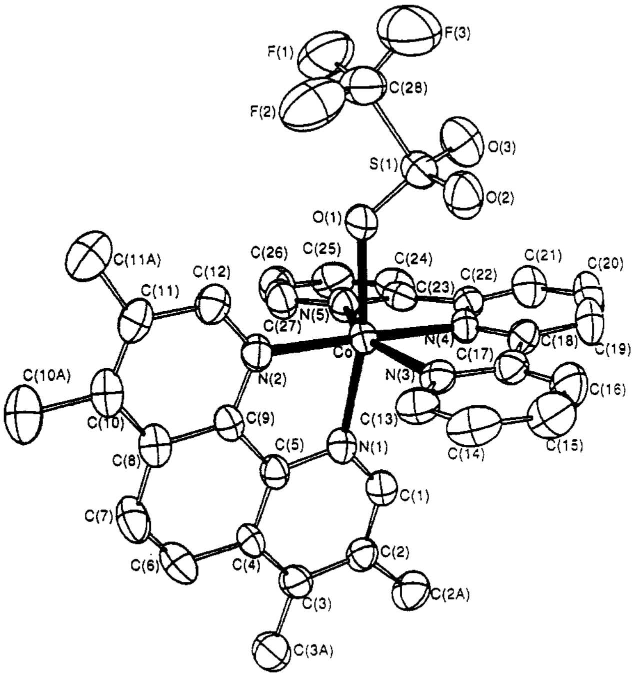

Figure 3. Structure of the complex (2+) cation in [Co(terpy)(3,4,7,8-tetramethyl-1,10-phenanthroline)(CF_3SO_3)]CF_3SO_3 (**7**). The second triflate (not shown) in separated from the cation by at least 4.83 Å (closest approach of a fluorine atom of this triflate to cobalt).

In parallel with these experiments, changes were monitored for the same solution under nonrigorously dry conditions (laboratory atmosphere). The much faster observed deactivation rate as shown in the two lower curves (dotted line) in Figure 4 is ascribed to the presence of adventitious moisture.

In related trials, a 10^{-3} M solution of **5** in dry nitrobenzene kept for 60 days at 25 °C under dioxygen retained 65% of its original activity, as measured by UV/visible spectroscopy. To mitigate the effect of suspected residual adventitious water, the experiment was repeated using a much more concentrated, 0.1 M solution of the complex. Remarkably, under the same conditions a 90% retention of activity was realized: this cor-

---

(15) Reichardt, C. *Solvents and Solvent Effects in Organic Chemistry*; VCH: Weinheim, FRG, 1988; p 20.

(16) See: Niederhoffer, E. C. Ph.D. Thesis Texas A&M University, 1983 (UMI Dissertation Services, Ann Arbor, MI) for results of studies of the decomposition of various cobalt polypyridine complexes in aqueous media.

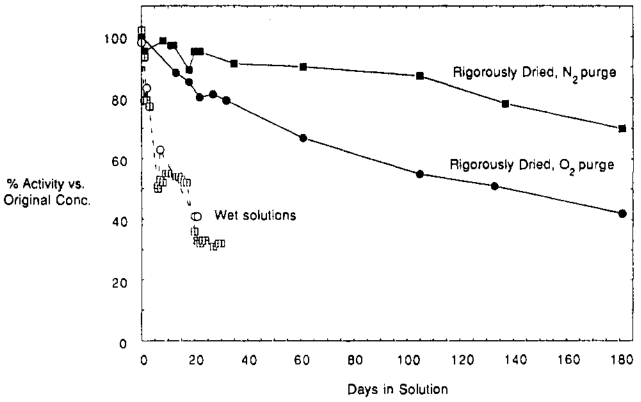

Figure 4. Results of stability studies on nitrobenzene solutions of [Co(terpy)(4,7-diphenyl-1,10-phenanthroline)(CF_3SO_3)]CF_3SO_3 under N_2 and O_2 (1 atm). Reversibly O_2-binding activity as a function of original concentration: under rigorously dry conditions; without rigorous drying of gases and solvent.

responds to a projected half-life of 8 months. With the possible exception of the Co(II) bis(TREN) complex,[17] we know of no other solution-phase O_2 carrier with this degree of longevity.

Since these stability studies showed that decomposition of the present Co(II) polypyridine complexes occurs to a significant extent by solvent- or water-induced chemistry, we attempted to reverse this process. A solution of $[Co(terpy)(bpy)]^{2+}$ (**1**) in undistilled nitrobenzene also containing 0.1 M tetrabutylammonium triflate was kept in contact with ambient air for 79 days which led to its extensive decomposition to a Co(II) O_2-inactive species having an $E_{1/2}$ of −0.02 V with a remaining very minor O_2-active component (**2**) at an $E_{1/2}$ of 0.33 V. The light yellow solution was heated (for 15 min) under dinitrogen and then allowed to cool with exposure to ambient air. A dark colored solution resulted which by its UV/vis spectrum (670-mm absorption) and CV analyses was shown to have a significantly increased concentration of $[Co(terpy)(bipy)]_2O_2{}^{4+}$ (cation of **2**). From measurements of the peak currents of the observed reversible waves at −0.02 and 0.33 V, it was calculated that 46% of the starting O_2-inactive complex had been converted to $[Co(terpy)(bpy)]^{2+}$ (cation of **2**).

A similar regeneration was seen for a partially degraded nitrobenzene solution of $[[Co(terpy)(4,7\text{-diphenyl-1,10-phenanthroline})]_2O_2](CF_3SO_3)_4$ (**5**) having 50% residual activity. Heating to 150 °C under N_2 followed by cooling in air resulted (by UV/vis analyses) in a partial regeneration to a 70% O_2-active solution. This partial "renewal" of the O_2-sorbent solutions might be ascribed to a thermal dissociation of coordinated water or resulting from a favorable ligand rearrangement to the active cobalt(II) species driven by the formation of its dioxygen complex.

Acknowledgment. We are grateful to D. Krause for technical assistance, to Dr. G. Johnson for the vibrational spectroscopy studies, and to Dr. B. Toby for discussions on the X-ray work. We also acknowledge the support and continued encouragement of Drs. J. Roth and T. Manuel and thank Air Products and Chemicals for permission to publish this work. Special thanks are due to K. Lakatosh for preparing this manuscript.

Supplementary Material Available: Listings of complete atomic coordinates and thermal parameters, anisotropic thermal parameters, and bond lengths and bond angles for **2a** and **7**, unit cell packing diagrams for **2a** and **7**, and text giving a detailed description of the structure of **7** (13 pages). Ordering information is given on any current masthead page.

---

[17] Motekaitis, R. J.; Martell, A. E. *J. Am. Chem. Soc.* **1988**, *110*, 7715.