

## Cyclic voltammetric studies of dioxygen-bridged dinuclear cobalt(III) complexes<sup>§</sup>

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**Abstract.** Cyclic voltammetric studies were carried out for dioxygen-bridged dinuclear cobalt(III) complexes using platinum electrodes at different values of pH and ionic strength. Reversible electrode reactions occur particularly for the dioxygen complexes  $[(\text{phen})_2\text{Co}(\mu\text{-O}_2, \text{NH}_2)\text{Co}(\text{phen})_2](\text{ClO}_4)_4 \cdot 2\text{H}_2\text{O}$  and  $[(\text{bpy})_2\text{Co}(\mu\text{-O}_2, \text{NH}_2)\text{Co}(\text{bpy})_2](\text{ClO}_4)_4 \cdot \text{H}_2\text{O}$  with 1,10-phenanthroline (phen) and 2,2-bipyridine (bpy) as the non-bridging ligands. For complexes with ammonia ( $\text{NH}_3$ ) ethylenediamine (en) as the terminal ligands, there is quasi-reversible electrode behaviour at  $\text{pH} < 3$  due to protonation of the peroxo complexes which subsequently undergo equilibration with isomeric forms. Such behaviour is well-marked for the peroxo complex  $[(\text{en})_2\text{Co}(\mu\text{-O}_2, \text{NH}_2)\text{Co}(\text{en})_2](\text{NO}_3)_3$ . The decaammine complex  $[(\text{NH}_3)_5\text{Co}(\mu\text{-O}_2)\text{Co}(\text{NH}_3)_5](\text{NO}_3)_5$  shows only a cathodic peak due to intramolecular charge transfer decomposition in solution after reduction at the electrode. Diffusion coefficients for all the dioxygen complexes were determined from the plots of  $I_p$  vs.  $\nu^{1/2}$ .

**Keywords.** Cyclic voltammetric studies; dioxygen-bridged dinuclear Co(III) complexes; superoxo complexes; peroxo complexes; coordinated dioxygen systems.

### 1. Introduction

Redox behaviour of dioxygen molecule in aqueous solution at different values of pH has been studied in great detail (Sawyer and Valentine 1981). It is of immense interest to study the electrodic behaviour of coordinated dioxygen systems for understanding the mechanisms of oxygenation and related biological redox reactions (McLendon and Martell 1976; Jones *et al* 1979). Considerable attention has been paid recently to these dioxygen coordinated metal complexes, since vital biological functions such as oxygen transport and many enzymatic reactions take place involving oxygen in different oxidation states (Wilkins 1971; Hayaishi 1975). Although the existence of cobalt complexes coordinated to dioxygen has been known for a long time, no specific biological functions are attributed to these species (Sykes and Weil 1970; Lever and Gray 1978). Depending upon the ligands and the conditions of oxygenation, the cobalt(II) ion forms 1:1 or 1:2 oxygen metal complexes (Basolo *et al* 1975; Jones *et al* 1979). Complexes of these types have been isolated and characterized with reference to structure, spectra and reactivity (Sykes and Weil 1970; McLendon and Martell 1976; Lever and Gray 1978; Jones *et al* 1979). Structural investigation and ESR studies of these dioxygen complexes show that the dioxygen moiety in these complexes exists in two forms namely peroxo (diamagnetic) and superoxo (paramagnetic) forms, the unpaired

<sup>§</sup> Dedicated to Prof. K S G Doss on his eightieth birthday.

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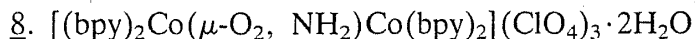
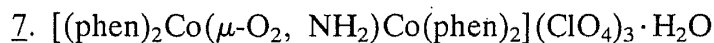
electron mainly resides in the superoxo group and the two cobalt atoms are equivalent (Sykes and Weil 1970; Lever and Gray 1978).

Electron transfer reactions of the superoxo complexes with a variety of one-electron reductants have been reported earlier and in all those reactions the redox reactions are known to occur at the dioxygen bridge and not at the cobalt centre (Sykes and Weil 1970; Sykes 1974; Lever and Gray 1975). Recently, electron transfer reactions of superoxo complexes with strong reducing agents such as excited  $\text{Ru}(\text{bpy})_3^{2+}$  and  $\text{Ru}(\text{phen})_3^{2+}$  ions (Chandrasekaran and Natarajan 1980, 1981), unstable metal ions (Natarajan and Raghavan 1980a), organic radicals (Natarajan and Raghavan 1981) and free superoxide ion (Natarajan and Raghavan 1980b) have been reported and in all those reactions the products are the corresponding peroxo complexes. Redox process of these dioxygen complexes with  $\text{Fe}^{2+}$ ,  $\text{Co}(\text{bpy})_3^{2+}$ ,  $\text{Co}(\text{phen})_3^{2+}$ ,  $\text{Fe}(\text{phen})_3^{2+}$  and the peroxo complex,  $[(\text{en})_2\text{Co}(\mu\text{-O}_2, \text{NH}_2)\text{Co}(\text{en})_2]^{3+}$  occur by an outer-sphere electron transfer mechanism (Sykes 1974; Chandrasekaran and Natarajan 1980). Recently, attempts have been made to calculate the self exchange rate constants for the superoxo/peroxo couples using the Marcus relationship (Michelson *et al* 1977; McLendon and Mooney 1980; Chandrasekaran and Natarajan 1981). In order to calculate the above self exchange rate constants, a systematic study of the thermodynamics of interconversion of  $\mu$ -superoxo and  $\mu$ -peroxo complexes in terms of fairly accurate reduction potentials, ( $E$  values vs. normal hydrogen electrode) is required. Vleck (1960) and Hanslik and Vleck (1973) reported polarographic reduction of  $\mu$ -superoxo complexes while Martell and co-workers (Harris *et al* 1980) employed cyclic voltammetry to determine the peak potentials for the oxidation of the peroxo complexes to the corresponding superoxo complexes. The observed redox potentials are interpreted in terms of metal-dioxygen bonding and the concept of charge-transfer from cobalt(II) to the dioxygen ligand. McLendon and Mooney (1980) and later Richens and Sykes (1982) have studied the electrodic reduction of some of the superoxo complexes using Pt electrodes in aqueous media. In the present investigation detailed cyclic voltammetric studies have been carried out for both the superoxo and the peroxo complexes by changing the ionic strength and pH of the solution. Cyclic voltammetry provides redox potentials as well as more information about the mechanistic details of electrode reactions of these complexes.

## 2. Experimental

Cyclic voltammetric studies were carried out for the following  $\mu$ -superoxo and  $\mu$ -peroxo complexes.

1.  $[(\text{NH}_3)_5\text{Co}(\mu\text{-O}_2)\text{Co}(\text{NH}_3)_5](\text{NO}_3)_5$
2.  $[(\text{NH}_3)_4\text{Co}(\mu\text{-O}_2, \text{NH}_2)\text{Co}(\text{NH}_3)_4](\text{NO}_3)_4$
3.  $[(\text{en})_2\text{Co}(\mu\text{-O}_2, \text{NH}_2)\text{Co}(\text{en})_2](\text{NO}_3)_4$
4.  $[(\text{phen})_2\text{Co}(\mu\text{-O}_2, \text{NH}_2)\text{Co}(\text{phen})_2](\text{ClO}_4)_4 \cdot 2\text{H}_2\text{O}$
5.  $[(\text{bpy})_2\text{Co}(\mu\text{-O}_2, \text{NH}_2)\text{Co}(\text{bpy})_2](\text{ClO}_4)_4 \cdot \text{H}_2\text{O}$
6.  $[(\text{en})_2\text{Co}(\mu\text{-O}_2, \text{NH}_2)\text{Co}(\text{en})_2](\text{NO}_3)_3$



The superoxo complexes 1–3 were prepared using the literature method (Davies *et al* 1972). Complexes 4–8 were prepared using the methods already reported with modifications (Mori and Weil 1967, 1968; Sasaki and Fujita 1969, 1970; Davies and Sykes 1971; Gileadi *et al* 1975). The dioxygen complexes were characterized by UV and visible spectra after recrystallization. A Hitachi Model 320 UV-visible spectrophotometer was used for spectral measurements. Cyclic voltammograms were run using PAR model 173 potentiostat/galvanostat. A PAR model 175 universal programmer was used to generate the cyclic triangular wave. Current output was monitored using PAR model 176 current follower. A Perkin-Elmer Hitachi 057 X-Y recorder was used for recording the cyclic voltammograms. The electrochemical cell was a three-electrode cell, cylindrical in shape with two sockets in which were inserted the working electrode and the counter electrode. The working electrode and the counter electrodes were platinum foils of one cm<sup>2</sup> area. A saturated calomel electrode placed in the side arm was the reference electrode and was connected to the potentiostat through a electrometer probe. Electrolytic contact was made by a luggin capillary projecting towards the working electrode. The platinum electrodes were cleaned and electrochemically treated prior to running a cyclic voltammogram. The condition of the working electrode was ascertained by running a cyclic voltammogram in 0.5 M H<sub>2</sub>SO<sub>4</sub> in the range +1.3 and –0.2 V vs. SCE at a potential scan rate of 50 mV/sec and compared with that reported in the literature (Sawyer and Roberts 1974; Gileadi *et al* 1975). The reagents hydrochloric acid, nitric acid, sulphuric acid, sodium nitrate, sodium sulphate and sodium perchlorate were AnalaR grade supplied by BDH or E Merck.

Cyclic voltammograms were run in aqueous media at 25°C. The solutions for the cyclic voltammetric experiments contained usually  $1 \times 10^{-3}$  M of the dioxygen-bridged dicobalt(III) complex in  $1 \times 10^{-3}$  M acid and 0.1 M supporting electrolyte. The acids used were perchloric acid, sulphuric acid, nitric acid and hydrochloric acid, and the supporting electrolytes were sodium perchlorate, sodium sulphate, sodium nitrate and potassium chloride, respectively. Solutions were deoxygenated by passing a stream of oxygen-free N<sub>2</sub> gas through the solution kept in the cell for 30 minutes prior to the potential sweep. Potential sweeps were carried out in the cathodic direction for superoxo complexes and in the anodic direction for peroxo complexes at scan rates ( $\nu$ ) 5 to 200 mV/sec. Experiments were carried out by varying the acidity and ionic strength for all the dioxygen complexes. Measured reduction potentials ( $E_{ob}$ ) were the mean values of the anodic ( $E_{pa}$ ) and cathodic ( $E_{pc}$ ) peak potentials at a given scan rate. The potential values mentioned hereafter are with reference to the normal hydrogen electrode (NHE) at 25°C.

### 3. Results

$\mu$ -Superoxo complexes are stable in solution with pH < 3 while the  $\mu$ -peroxo complexes are stable in neutral or alkaline solution. In the case of  $\mu$ -peroxo complexes 7 and 8 the complexes are stable even at pH = 1 without appreciable protonation of the peroxo group. Protonation is said to be absent in  $\mu$ -superoxo

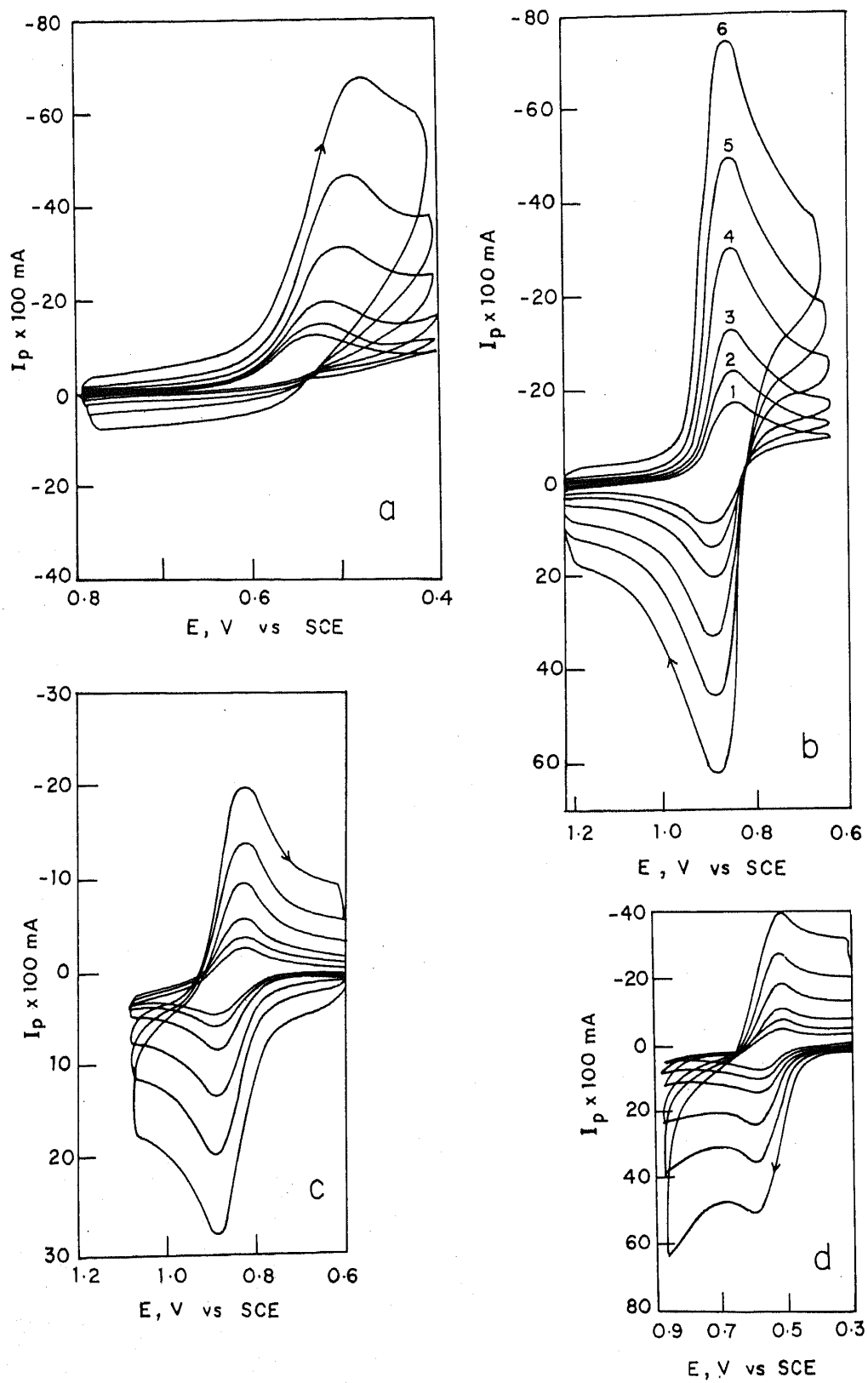
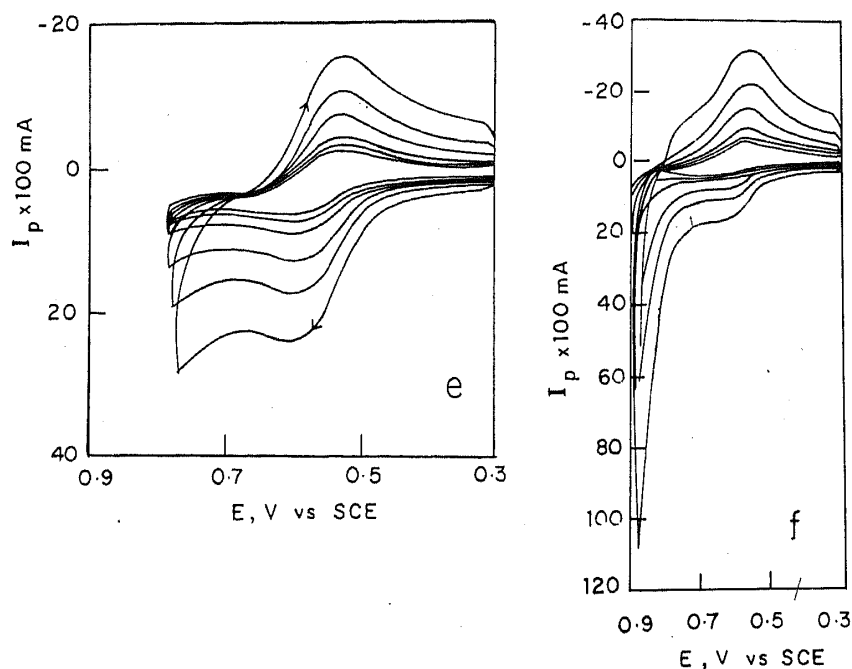


Figure 1. a,b,c,d.



**Figure 1.** Cyclic voltammograms of dioxxygen-bridged dicobalt(III) complexes at scan rates 5, 10, 20, 50, 100 and 200 mV/sec. (a)  $[(\text{NH}_3)_5\text{Co}(\mu\text{-O}_2)\text{Co}(\text{NH}_3)_5](\text{NO}_3)_5$  in 0.05 M  $\text{HClO}_4$ ;  $[\text{complex}] = 1.185 \times 10^{-3}$  M;  $[\text{NaClO}_4] = 0.1$  M. (b)  $[(\text{bpy})_2\text{Co}(\mu\text{-O}_2, \text{NH}_2)\text{Co}(\text{bpy})_2](\text{ClO}_4)_4 \cdot \text{H}_2\text{O}$  in 0.2 M  $\text{HNO}_3$ ;  $[\text{complex}] = 2.009 \times 10^{-3}$  M;  $[\text{KNO}_3] = 0.1$  M. (c)  $[(\text{bpy})_2\text{Co}(\mu\text{-O}_2, \text{NH}_2)\text{Co}(\text{bpy})_2](\text{ClO}_4)_3 \cdot 2\text{H}_2\text{O}$  in 0.01 M  $\text{H}_2\text{SO}_4$ ;  $[\text{complex}] = 5 \times 10^{-4}$  M;  $[\text{Na}_2\text{SO}_4] = 0.1$  M. (d)  $[(\text{en})_2\text{Co}(\mu\text{-O}_2, \text{NH}_2)\text{Co}(\text{en})_2](\text{NO}_3)_3$  in  $1 \times 10^{-3}$  M  $\text{HClO}_4$ ;  $[\text{complex}] = 1.007 \times 10^{-3}$  M;  $[\text{NaClO}_4] = 0.1$  M. (e)  $[(\text{en})_2\text{Co}(\mu\text{-O}_2, \text{NH}_2)\text{Co}(\text{en})_2](\text{NO}_3)_3$  in 0.1 M  $\text{HClO}_4$ ;  $[\text{complex}] = 9.3 \times 10^{-4}$  M;  $[\text{NaClO}_4] = 0.1$  M. (f)  $[(\text{en})_2\text{Co}(\mu\text{-O}_2, \text{NH}_2)\text{Co}(\text{en})_2](\text{NO}_3)_3$  in 1.0 M  $\text{HClO}_4$ ;  $[\text{complex}] = 9.83 \times 10^{-4}$  M;  $[\text{NaClO}_4] = 0.1$  M.

complexes (Sykes and Weil 1970; Lever and Gray 1978). The  $\mu$ -peroxo complex **6** in acidic solutions undergoes isomerization reaction after fast protonation and this protonation equilibrium has been studied in considerable detail (Sykes and Weil 1970; Lever and Gray 1978). There is no observable decomposition of the dioxxygen complexes during the course of the study in the media in which cyclic voltammetric experiments were carried out as is determined from the UV and visible absorption spectra. Typical cyclic voltammograms of the dioxxygen complexes are given in figure 1. The values of peak potentials ( $E_p$ ), peak currents ( $I_p$ ) and separation in peak potentials ( $E_p$ ) were measured in all cases from the cyclic voltammograms recorded at different potential sweep rates (Nicholson and Shain 1964; Sawyer and Roberts 1974) (table 1). For a reversible electrode couple, the peak current is related to the potential scan rate and the concentration of the complex by the expression (Nicholson and Shain 1964; Sawyer and Roberts 1974; Gileadi *et al* 1975),

$$|I_p| = 2.72 \times 10^5 n^{3/2} D^{1/2} C_0 \nu^{1/2},$$

where  $I_p$  = peak current in amperes;  $D$  = diffusion coefficient in  $\text{cm}^2/\text{sec}$ ;  $n$  = number of electrons involved in the electrode process,  $C_0$  = concentration of the complex in moles/litre and  $\nu$  = potential scan rate in volts/sec. Plots of  $I_{pc}$  or  $I_{pa}$

**Table 1a.** Peak potentials and peak currents at different scan rates for the complex  $[(\text{NH}_3)_5\text{Co}(\mu\text{-O}_2)\text{Co}(\text{NH}_3)_5](\text{NO}_3)_5$ .

$\nu$ (mV/sec)	$E_p$ (V) vs. NHE	$I_p$ ( $\mu$ A)	$I_p/\nu^{1/2}$
5	0.788	95	42.5
10	0.778	130	41.1
20	0.768	180	40.3
50	0.758	280	39.6
100	0.747	410	41.0
200	0.735	560	39.6

$[\text{HClO}_4] = 0.05$  M;  $[\text{NaClO}_4] = 0.1$  M; [Complex]  
 $= 1.185 \times 10^{-3}$  M; sweep range = +0.8 to +0.4 V.

**Table 1b.** Peak potentials, peak currents and difference in peak potentials at different scan rates for the complex  $[(\text{phen})_2\text{Co}(\mu\text{-O}_2, \text{NH}_2)\text{Co}(\text{phen})_2](\text{ClO}_4)_4 \cdot \text{H}_2\text{O}$ .

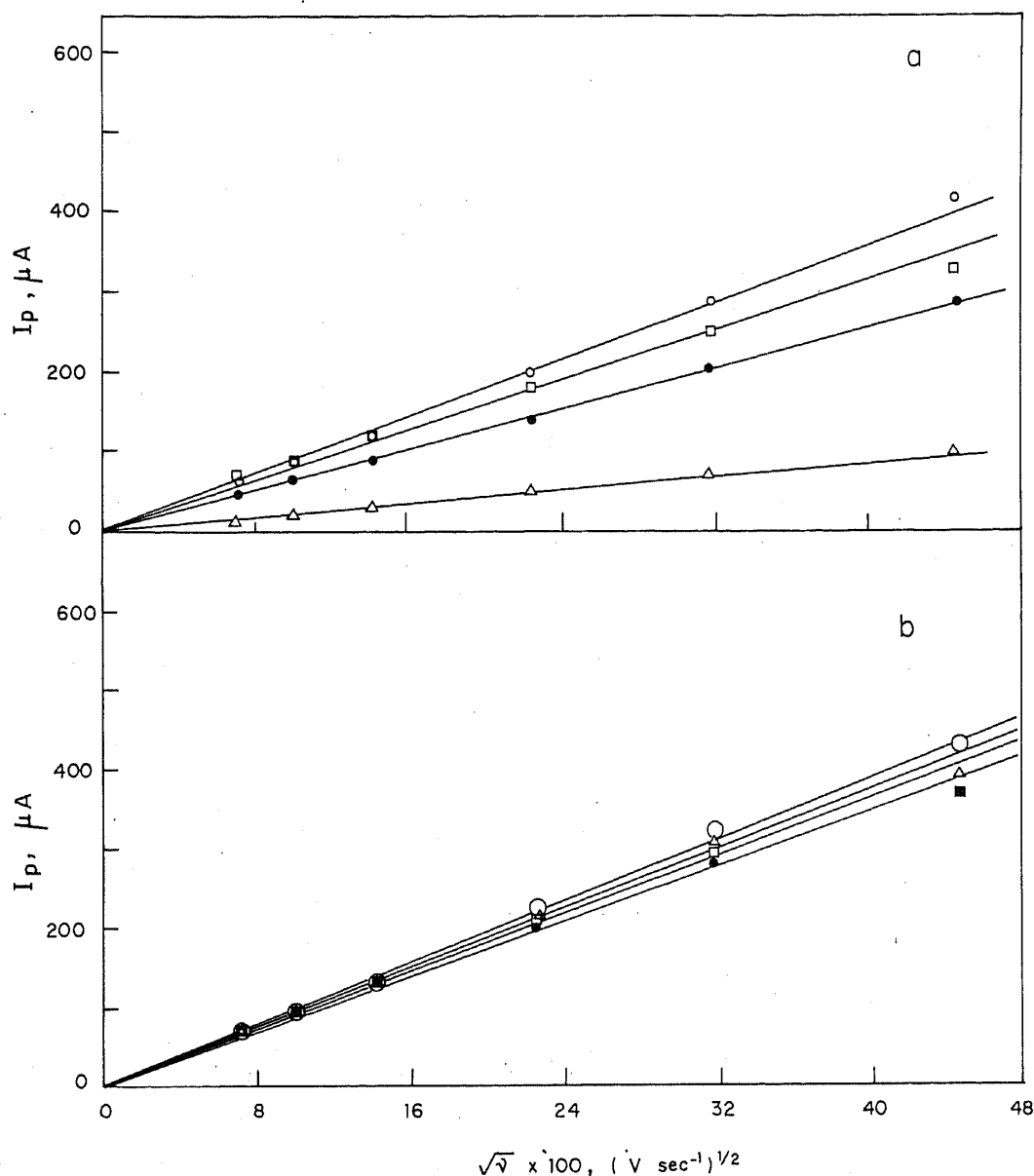
$\nu$ (mV/sec)	$E_p$ (V) vs. NHE	$\Delta E_p$ (mV)	$I_{pa}$ ( $\mu$ A)	$I_{pc}$ ( $\mu$ A)	$I_{pa}/\nu^{1/2}$	$I_{pc}/\nu^{1/2}$	$I_{pa}/I_{pc}$
5	1.073	55	70	70	31.25	31.25	1.00
10	1.073	55	100	100	31.65	31.65	1.00
20	1.073	55	130	130	29.08	29.08	1.00
50	1.073	55	205	220	29.00	31.12	0.95
100	1.073	55	290	320	29.00	32.00	0.91
200	1.073	55	370	430	26.17	30.41	0.86

$[\text{H}_2\text{SO}_4] = 0.1$  M;  $[\text{Na}_2\text{SO}_4] = 0.1$  M; [complex] =  $1.014 \times 10^{-3}$  M; sweep rate = +1.2 to +0.6 V.

vs.  $\nu^{1/2}$  are linear for complexes 2 to 8 in weakly acidic solutions (figure 2) and from the slopes of the above plots, the values of the diffusion coefficients were calculated. The values of peak potentials ( $E_p$ ), separation of peak potentials ( $\Delta E_p$ ) and the values of diffusion coefficient ( $D$ ) are tabulated (tables 2a–e) for complexes 2 to 8 at different acidities and ionic strengths of the medium. Redox potentials of the superoxo-bridged complexes at pH = 1 or 3 determined in the present investigation are shown in table 3.

#### 4. Discussion

The peroxo ion having two electrons in the  $\pi_{2p}$  antibonding level is the least stable among the dioxygen species. In aprotic media, the peroxide dianion is a highly unstable species. When protons or metal ions stabilize the peroxide dianion the redox potentials are known to be altered (Sawyer and Valentine 1981). When the peroxide ion is coordinated to a metal ion, the stability increases as there is withdrawal of electronic charge from the peroxo group. Conversion of a superoxo to a peroxo complex is a thermodynamically favourable reaction.



**Figure 2a.**  $I_p$  vs.  $\nu^{1/2}$  plots for the complex  $[(en)_2Co(\mu-O_2, NH_2)Co(en)_2](NO_3)_3$ . (i)  $[complex] = 1.007 \times 10^{-3}$  M;  $[HClO_4] = 1 \times 10^{-3}$  M;  $[NaClO_4] = 0.1$  M;  $\circ - I_{pa}$  vs.  $\nu^{1/2}$ ;  $\square - I_{pc}$  vs.  $\nu^{1/2}$ . (ii)  $[complex] = 0.983 \times 10^{-3}$  M;  $[HClO_4] = 1.0$  M;  $[NaClO_4] = 0.1$  M;  $\triangle - I_{pa}$  vs.  $\nu^{1/2}$ . (iii)  $[complex] = 0.930 \times 10^{-3}$  M in 75%  $CH_3CN$ ;  $[NaCl] = 0.1$  M;  $\bullet - I_{pa}$  vs.  $\nu^{1/2}$ . (b) (i)  $[(phen)_2Co(\mu-O_2, NH_2)Co(phen)_2](ClO_4)_4$ ;  $[complex] = 1.005 \times 10^{-3}$  M;  $[H_2SO_4] = 0.1$  M;  $[Na_2SO_4] = 0.1$  M;  $\circ - I_{pc}$  vs.  $\nu^{1/2}$ ;  $\square - I_{pa}$  vs.  $\nu^{1/2}$ . (ii)  $[(phen)_2Co(\mu-O_2, NH_2)Co(phen)_2](ClO_4)_3$ ;  $[complex] = 1.002 \times 10^{-3}$  M;  $[HNO_3] = 0.1$  M;  $[KNO_3] = 0.1$  M;  $\triangle - I_{pa}$  vs.  $\nu^{1/2}$ ;  $\bullet - I_{pc}$  vs.  $\nu^{1/2}$ .

The superoxo complexes 2 to 5 and the peroxo complexes 6, 7 and 8 show reversible one-electron transfer process at the electrode. The apparent deviation from the reversibility of the superoxo complexes 2, 3 and 6 at higher acidity is explained on the basis of the protonation of the peroxo species in homogeneous solution. The absence of anodic peak for the ammine complex 1 in 0.05 M  $HClO_4$  can be attributed either to the slow heterogeneous electron transfer of the reduced

**Table 2b.** Peak potentials, difference in peak potentials and diffusion coefficients for the complex  $[(en)_2Co(\mu-O_2, NH_2)Co(en)_2](NO_3)_3$  at different  $[H^+]$ .

$[HClO_4](M)$	$E_p(V)$ vs. NHE	$\Delta E_p(mV)$	$D \times 10^6$ ( $cm^2/sec$ )
0.001	0.774	70	10.030
0.100	0.778	60	2.238
1.000	0.818	56	0.715
*75% $CH_3CN$	0.773	60	6.053

$\nu = 50$  mV/sec; [complex] =  $1 \times 10^{-3}$  M; sweep range = +0.3 V to +0.9 V;

\* [complex] =  $9.30 \times 10^{-4}$  M; supporting electrolyte = 0.1 M NaCl.

**Table 2a.** Peak potentials, difference in peak potentials and diffusion coefficients for the complex  $[(en)_2Co(\mu-O_2, NH_2)Co(en)_2](NO_3)_4$  at different  $[H^+]$  and ionic strength.

[Medium](M)		$E_p$ (V) vs. NHE	$\Delta E_p$ (mV)	$D \times 10^5$ (cm <sup>2</sup> /sec)
H <sup>+</sup>	Supporting electrolyte			
HClO <sub>4</sub>				
0.0005	0.1	0.770	63	1.868
0.0010	0.1	0.773	63	1.668
0.0050	0.1	0.768	66	1.512
0.0100	0.1	0.773	71	2.164
0.5000	0.1	0.810	73	2.138
0.0010	0.05	0.778	65	1.515
0.0010	0.20	0.766	62	1.515
0.0010	0.40	0.763	65	1.415
H <sub>2</sub> SO <sub>4</sub>				
0.0005	Na <sub>2</sub> SO <sub>4</sub> 0.1	0.708	60	1.719
0.0010	0.1	0.713	62	1.714
0.0025	0.1	0.708	70	1.647
0.0010	0.05	0.703	65	1.450
0.0010	0.4	0.683	65	1.258

$\nu = 50$  mV/sec; [complex] =  $1 \times 10^{-3}$  M; sweep range = +0.8 to +0.35 V.



**Table 2d.** Peak potentials, difference in peak potentials and diffusion coefficients for the complex [(bpy)<sub>2</sub>Co(μ-O<sub>2</sub>, NH<sub>2</sub>)Co(bpy)<sub>2</sub>](ClO<sub>4</sub>). H<sub>2</sub>O at different [H<sup>+</sup>] and ionic strength.

[Medium] (M)				
H <sup>+</sup>	Supporting electrolyte	E <sub>p</sub> (V) vs. NHE	ΔE <sub>p</sub> (mV)	D × 10 <sup>5</sup> (cm <sup>2</sup> /sec)
HNO <sub>3</sub>	KNO <sub>3</sub>			
0.1	0.1	1.036	62	1.511
0.2	0.1	1.050	64	1.549
0.3	0.1	1.043	62	1.563
0.4	0.1	1.036	65	1.541
1.0	0.1	1.033	62	1.518
H <sub>2</sub> SO <sub>4</sub>	Na <sub>2</sub> SO <sub>4</sub>			
0.050	0.1	1.078	55	1.376
0.100	0.1	1.068	55	1.277
0.200	0.1	1.058	60	1.352
0.300	0.1	1.048	60	1.300
0.400	0.1	1.028	60	1.222
1.000	0.1	1.003	60	1.145
0.1	—	1.076	58	1.274
0.1	0.02	1.076	58	1.196
0.1	0.50	1.068	55	1.088
0.1	1.00	1.040	58	0.927

$\nu = 50$  mV/sec; [complex] =  $1 \times 10^{-3}$  M; sweep range = +1.2 to 0.6 V.

**Table 2c.** Peak potentials, difference in peak potentials and diffusion coefficients for the complex [(phen)<sub>2</sub>Co(μ-O<sub>2</sub>, NH<sub>2</sub>)Co(phen)<sub>2</sub>](ClO<sub>4</sub>)<sub>3</sub>. H<sub>2</sub>O at different [H<sup>+</sup>] and ionic strength.

[Medium] (M)				
H <sup>+</sup>	Supporting electrolyte	E <sub>p</sub> (V) vs. NHE	ΔE <sub>p</sub> (mV)	D × 10 <sup>5</sup> (cm <sup>2</sup> /sec)
HNO <sub>3</sub>	KNO <sub>3</sub>			
0.001	0.1	1.088	59	1.420
0.010	0.1	1.086	58	1.278
0.110	0.1	1.075	60	1.147
0.210	—	1.060	60	1.188
0.410	—	1.040	59	1.226
1.100	—	1.010	65	1.352
H <sub>2</sub> SO <sub>4</sub>	Na <sub>2</sub> SO <sub>4</sub>			
0.001	0.1	1.088	57	1.242
0.020	0.1	1.083	57	1.117
0.120	0.1	1.053	57	1.147
0.010	—	1.108	60	1.114
0.020	—	1.088	60	1.117
0.110	—	1.063	59	1.077
0.210	—	1.058	55	1.147
0.410	—	1.043	58	1.077
1.000	—	1.008	62	0.959

$\nu = 50$  mV/sec; [complex] =  $5 \times 10^{-4}$  M; sweep range = 0.6 to 1.1 V.

**Table 2e.** Peak potentials, difference in peak potentials and diffusion coefficients for the complex  $[(bpy)_2Co(\mu-O_2,NH_2)Co(bpy)_2](ClO_4)_3 \cdot 2H_2O$  at different  $[H^+]$  and ionic strength.

[Medium] (M)		$E_p$ (V) vs. NHE	$\Delta E_p$ (mV)	$D \times 10^5$ (cm <sup>2</sup> /sec)
$H^+$	Supporting electrolyte			
$HNO_3$	$KNO_3$			
0.001	0.1	1.083	55	1.183
0.010	0.1	1.078	62	1.374
0.200	0.1	1.060	60	1.398
0.400	—	1.033	62	1.219
$H_2SO_4$	$Na_2SO_4$			
0.001	0.1	1.081	58	1.293
0.010	0.1	1.078	56	1.227
0.010	—	1.123	55	1.188
0.100	—	1.081	58	1.117
0.200	—	1.061	60	1.250
0.400	—	1.045	60	1.156

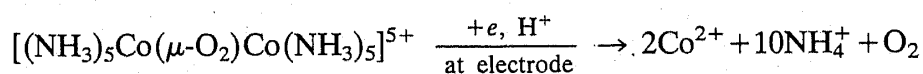
$\nu = 50$  mV/sec; [complex] =  $1 \times 10^{-3}$  M; sweep range = +0.6 to +1.1 V

**Table 3.** Redox potentials of  $\mu$ -superoxo bridged dinuclear cobalt(III) complexes.

Complex	pH	$E$ (V) vs. NHE
<u>1</u>	1	$0.760 \pm 0.005$
<u>2</u>	3	$0.763 \pm 0.005$
<u>3</u>	3	$0.800 \pm 0.010$
<u>3</u>	3	$0.725^* \pm 0.010$
<u>4</u>	1	$1.100 \pm 0.010$
<u>5</u>	1	$1.095 \pm 0.010$

\* In solution containing  $SO_4^{2-}$  ions.

species at the electrode or to a quasi-reversible reaction; chemical reaction followed by electrodic reduction of the superoxo complex. Decomposition of the superoxo complex 1 in aqueous acidic medium has also been reported in the reduction of the complex using  $Fe^{2+}$  as the reductant. In a similar way for complex 1 there is fast protonation of the peroxo complex formed at the electrode in the reduction process which subsequently undergoes charge transfer decomposition as follows.



Barnartt and Charles (1962) observed quantitative evolution of oxygen when this complex underwent reduction at platinum electrode. Unlike the above monobridged superoxo complex, the following monobridged complexes [(en)

(dien)Co( $\mu$ -O<sub>2</sub>)Co(dien)(en)]<sup>4+</sup> and [(trien)(NH<sub>3</sub>)Co( $\mu$ -O<sub>2</sub>)Co(NH<sub>3</sub>)(trien)]<sup>4+</sup> show reversible behaviour at the electrode under the same conditions (Jebaraj 1982). This indicates that the occurrence of the anodic peaks for the monobridged superoxo complexes depends on the stability of the protonated peroxo complexes towards intramolecular charge transfer decomposition.

$\mu$ -superoxo and  $\mu$ -peroxo complexes with non-bridging ligands NH<sub>3</sub>, en, bpy and phen in weakly acidic solution, ([H<sup>+</sup>] < 0.1 M) show reversible behaviour at electrodes. For the above systems (a)  $I_p/\nu^{1/2}$  is constant, (b)  $I_{pa}/I_{pc}$  is constant at all scan rates and (c)  $E_p$  is  $58 \pm 2$  mV ( $n = 1$ ) characteristic of reversible redox systems. On increasing the acidity there is an anodic shift of peak potentials ( $E_p$ ) particularly for the dibridged superoxo complexes 2 and 3 with NH<sub>3</sub> and (en) ligands, while increase of ionic strength with salts produces a slight cathodic shift of peak potentials. The observed increase in  $E_p$  (anodic shift) with increase in [H<sup>+</sup>] indicates that the peroxo analogue of 2 and 3 formed on reduction protonates readily in solution. The protonated species of the  $\mu$ -peroxo complexes exist in equilibrium after isomerization as follows (Mori and Weil 1967):

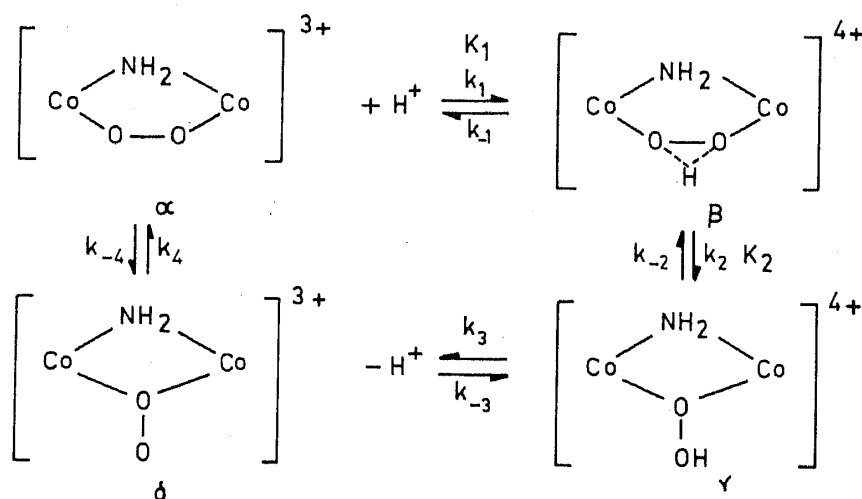


Chart 1.

Sykes and Weil (1970) studied the above equilibrium for the complex 6. The electrode phenomena of these complexes approach that of a quasi-reversible one where there is electrode reaction followed by fast homogeneous reaction when [H<sup>+</sup>] is increased. Once the  $\mu$ -superoxo complex undergoes reduction at the electrode there is fast protonation of the peroxo species in solution at the electrode. The species which undergo oxidation at the electrode are not only the unprotonated form of the peroxo complex but also the isomeric forms of the protonated peroxo complex. The concentration of each species that undergoes oxidation at the electrode surface is again determined by the equilibrium constants  $K_1$ ,  $K_2$  and [H<sup>+</sup>]. Richens and Sykes (1982) who observed such electrodic behaviour for these complexes on varying [H<sup>+</sup>] proposed the following correlation for the observed potentials and the formal potential

$$E_{\text{obs}} = E^0 + \frac{0.059}{n} \log \{1 + K_1(1 + K_2)[\text{H}^+]\}$$

where  $K_1$  and  $K_2$  are the equilibrium constants. For the complex 2, on increase of  $[H^+]$  from 0.001 M to 0.5 M using  $HClO_4$ , the observed potential shifts anodically from 0.763 to 0.820 V. While keeping the  $[H^+]$  at  $1 \times 10^{-3}$  M, increase of ionic strength using  $ClO_4^-$  or  $NO_3^-$  results in a small shift in  $E_p$  cathodically (table 2). In HCl medium also this complex shows redox potentials of 0.758 and 0.853 V at  $[H^+] = 0.001$  M and 1.0 M, respectively, while in 1.0 M NaCl it is 0.723 V. In a similar fashion, the complex 3 shows  $0.80 \pm 0.01$  V as the reduction potential in a solution at pH = 3 ( $HClO_4$  or HCl) whereas Richens and Sykes (1982) report a value of 0.863 V. The peroxo analogue of complex 6 also shows a value of 0.800 V in  $1 \times 10^{-3}$  M  $HClO_4$  and also in 90% acetonitrile (0.1 M NaCl supporting electrolyte). However, the superoxo complex 3 in  $1 \times 10^{-3}$  M  $H_2SO_4$  undergoes reduction at 0.725 V which is 75 mV more cathodic than that observed in  $1 \times 10^{-3}$  M  $HNO_3$  or  $HClO_4$ . This is presumably due to the ion-pair formation between the superoxo cation and the sulphate anion. The ion-pair then undergoes reduction at a potential more cathodic than the free superoxo ion. This type of cathodic shift has also been found for the peroxo complex 6 in acetonitrile medium when using  $Na_2SO_4$  as the supporting electrolyte.

Although the plot of  $I_p$  vs.  $\nu^{1/2}$  is linear for the peroxo complex 6, when  $[H^+]$  is varied from  $1 \times 10^{-3}$  to 1.0 M, it has been observed that the peak current values ( $I_p$ ) decrease with  $[H^+]$ . Consequently, there is apparent decrease in the value of the diffusion coefficient, calculated from the slope of  $I_p$  vs.  $\nu^{1/2}$  plot for  $[H^+]$  ranging from  $1 \times 10^{-3}$  to 1.0 M. Such a change in the diffusion coefficients is not seen with the superoxo complexes on varying  $[H^+]$ . This implies that the concentration ( $C_0$ ) used in the calculation of  $D$  from the slope ( $2.72 \times 10^5 n^{3/2} AD^{1/2} C_0$ ) is not the actual concentration of peroxo ions, which are electroactive, and the actual concentration of the electroactive species is slightly less than the concentration of the peroxo complex ( $C_0$ ) used in the calculation. Such a decrease in  $I_p$  with  $[H^+]$  is expected for this complex since with increase in  $[H^+]$ , there will be a shift in the protonation equilibrium towards the  $\gamma$ -form of the peroxo complex. It has been reported earlier that the  $\gamma$ -form of the peroxo complex does not undergo oxidation with  $Ce^{4+}$  or  $Fe(phen)_3^{3+}$  readily unlike the  $\alpha$ -form (Mori and Weil 1967). The  $\gamma$ -form of the peroxo complex is also expected to behave in a similar way at the electrode. The diffusion coefficient values at  $1 \times 10^{-3}$  M and 1.0 M  $[H^+]$  indicate that only 20% of the peroxo complex is electroactive form when  $[H^+] = 1.0$  M.

Unlike the complexes 2, 3 and 6, the complexes with non-bridging ligands bpy and phen (complexes 4, 5, 7 and 8) show quite reversible electrodic behaviour in both  $HNO_3$  and  $H_2SO_4$  media. There is no observable anodic shift of the peak potentials on varying  $[H^+]$ . On the other hand, there is a small cathodic shift of peak potentials on increasing the acidity or ionic strength (table 2). Further, there is no decrease in peak current with increase in  $[H^+]$  for the peroxo complex 7 and 8. The observed electrodic behaviour is understood to be due to the absence of protonation in the peroxo complexes 7 and 8.

There is no change in reduction potentials ( $E$ ) of the dioxygen complexes to start with in either the superoxo complex or its analogue. Reduction potential ( $E$ ) for the superoxo/peroxo complexes show considerable variation when the non-bridging ligands are varied (table 3). Such a variation in redox potential has also

been known for mononuclear cobalt(III) complexes on changing the ligands from (phen) to  $\text{CN}^-$ , the potentials are  $\text{Co(phen)}_3^{3+/2+} = 0.37$  (Pryzstas and Sutin 1973);  $\text{Co(bpy)}_3^{3+/2+} = 0.37$  (Paglia and Sironi 1957);  $\text{Co(en)}_3^{3+/2+} = 0.18$  (Kim and Rock 1969);  $\text{Co(NH}_3)_6^{3+/2+} = 0.108$ ;  $\text{Co(CN)}_5(\text{H}_2\text{O})^{2-/3-} = -0.43$  V. The ligands which stabilize the cobalt(II) complex for oxidation have higher redox potentials. Thus the redox potentials of cobalt(III) complexes increase when the degree of chelation of amine ligands increases. In superoxo/peroxo complexes also, the terminal ligands which induce electron withdrawal from the  $\text{O}_2$  bridge stabilize the bridge for oxidation. The dioxygen complexes with chelates (bpy) or (phen) with delocalization of  $\text{O}_2^-$  electrons in the molecular orbitals of the ligands have higher potential than the complexes with terminal ligands (en) and  $\text{NH}_3$ .

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