120. The Reactivity of the Pentacyano(η^1-Dioxygen)cobaltate(III) Ion in Aqueous Solution

by **Michel H. Gubelmann, Stéphane Rüttimann, Bernard Bocquet,** and **Alan F. Williams***

Department of Inorganic, Analytical, and Applied Chemistry, University of Geneva,
30, quai Ernest Ansermet, CH-1211 Genève 4

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The mononuclear η^1-dioxygen complex $[Co(CN)_5O_2]^{3-}$ (**A**) decomposes in aqueous solution to the hydroxo-complex $[Co(CN)_5OH]^{3-}$ (**B**) and the hydroperoxo complex $[Co(CN)_5OOH]^{3-}$ (**C**). The mechanism involves partial dissociation of **A** to give $[Co(CN)_5]^{3-}$ (**E**) which binds with unreacted **A** to give the η^1:η^1-peroxo complex $[(CN)_5CoO_2Co(CN)_5]^{6-}$ (**F**) which is hydrolysed to **B** and **C**. The mechanism is supported by the effects of pH, dioxygen concentration, and ionic strength on the rate of decomposition, and by the trapping of oxidation products of **E** and **F**. Complex **A** reacts readily with reducing agents to give directly the hydroperoxo complex **C**.

Introduction. – The mononuclear η^1-dioxygen complexes of cobalt have attracted attention for many years [1] as potential oxygen carriers, or as models for (η^1-dioxygen)iron complexes known to be present in biological systems [2] [3] and as potential oxidation catalysts [4] [5]. The greater part of published work has concentrated on the structural, mechanistic, and thermodynamic aspects of the formation of dioxygen complexes from molecular oxygen and a Co(II) complex:

$$[Co(II)L_5] + O_2 \rightleftharpoons [CoO_2L_5] \quad (1)$$

Much less attention has been paid to the reactivity of these complexes, principally because of their tendency to react with a second Co(II) species to give a binuclear (η^1:η^1-dioxygen)dicobalt species [6]:

$$[CoO_2L_5] + [Co(II)L_5] \rightleftharpoons [L_5CoO_2CoL_5] \quad (2)$$

In cases where the mononuclear complex $[CoO_2L_5]$ is known to be present, oxidation of hydroquinone, of thiols, of ascorbic acid, and of *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine (TMPD; *N,N,N′,N′*-tetramethyl-1,4-benzenediamine) has been reported [7], and either hydrogen-radical abstraction or one-electron oxidation proposed. Hydrogen-radical abstraction by mononuclear $[CoO_2L_5]$ complexes has frequently been postulated in catalytic mechanisms, and also in cases where autooxidation of an organic ligand bound to Co-atom has occurred [8].

This paper reports a study of the behaviour of the complex pentacyano(η^1-dioxygen)cobaltate(III), $[Co(CN)_5O_2]^{3-}$ (**A**) in aqueous solution. Complex **A** is a simple, readily prepared [9], η^1-dioxygen complex which is stable over a period of months as its tetraethylammonium salt, and, therefore, seemed an appropriate choice to investigate the behaviour of η^1-dioxygen complexes. An X-ray crystal-structure determination has confirmed it to be an η^1-dioxygen complex [10]. Complex **A** has been shown to react with substituted phenols [11], quinones [12], phenoxy radicals [13], and $MoCl_5$ [14], although the mechanisms of these reactions remain uncertain.

Results. – 1. *The UV/VIS Spectrum of* $[Co(CN)_5O_2]^{3-}$ (**A**) *in Aqueous Solution.* The absorption spectrum of **A** in aqueous solution is rather difficult to measure because of decomposition, but in conditions where this is extremely slow (0°, 1M NaOH, 1 atm of oxygen, see below), the spectrum shows a strong band at 310 nm ($7500 < \varepsilon < 8000 \text{M}^{-1} \cdot \text{cm}^{-1}$) with a well developed shoulder near 372 nm ($\varepsilon \approx 1600 \text{M}^{-1} \cdot \text{cm}^{-1}$). There is a weaker shoulder around 490 nm ($\varepsilon \approx 200 \text{M}^{-1} \cdot \text{cm}^{-1}$) which may, however, be due to traces of the binuclear μ-superoxo species $[(CN)_5CoO_2Co(CN)_5]^{5-}$ which is formed in these conditions (see below). Our spectral data are in reasonable agreement with the literature values of the absorption maxima for $[Co(CN)_5O_2]^{3-}$ in non-aqueous solvents [15], but the extinction coefficients we measure are significantly greater *(Table 1)*, and we suspect that this may be due to partial decomposition of the compound in previous work. We have found **A** to decompose in MeCN and DMF as found for aqueous solutions, the rate increasing with the amount of H_2O present in the solvent. The slight blue shift observed on moving from non-aqueous solvents to H_2O has also been observed for the binuclear $[(CN)_5CoO_2Co(CN)_5]^{5-}$ [15]. The assignments of the absorption bands in *Table 1* are taken from [15], and reflect the standard description of this complex as a superoxo complex of Co(III), in agreement with the EPR spectrum [15].

Table 1. *Spectral Data* (λ_{max} [nm], ε [$\text{M}^{-1} \cdot \text{cm}^{-1}$]) *for* $[Co(CN)_5O_2]^{3-}$ *in Various Solvents*

H_2O[a])	MeCN[b])	MeOH[b])	DMF[b])	Assignment[b])
490 (200)	530 (80)	510 (110)	520 (90)	MLCT
372 (1600)	400 (1000)	380 (900)	390 (1150)	d–d
310 (7750)	320 (2800)	315 (4600)	320 (4800)	LMCT

[a]) This work. [b]) From [15].

2. *Decomposition of* $[Co(CN)_5O_2]^{3-}$ (**A**) *in Aqueous Solution.* When $(Et_4N)_3[Co(CN)_5O_2] \cdot n\ H_2O$ is dissolved in H_2O, the following changes are observed: *i)* The pH of the solution rises, stabilising around pH 11 for a solution $3 \cdot 10^{-3}$ M in **A**. *ii)* In a closed system, the liberation of molecular oxygen is detected with an oxygen-sensitive electrode. *iii)* The absorption spectrum of the solution changes dramatically *(Fig. 1)* with the disappearance of the LMCT band at 310 and a decrease in absorbance of the d–d band at 372 nm. An isosbestic point is observed at *ca.* 282 nm, and a shoulder appears at 272 nm.

Titration of the solution with strong acid at the end of the reaction shows two end points at 0.5 and 1 equiv. of acid/cobalt, with apparent pK_a values of 10.6 and 6.5, respectively *(Fig. 2)*. The intensity of the 272-nm band is virtually unaffected during the first step of protonation, but decreases rapidly during the addition of the second 0.5 equiv. The spectrum of the solution after addition of 1 equiv. of acid is that of $[Co(CN)_5(OH_2)]^{2-}$ [16–18], and the solution has an oxidising power of 1 equiv./cobalt as shown by reaction with iodide.

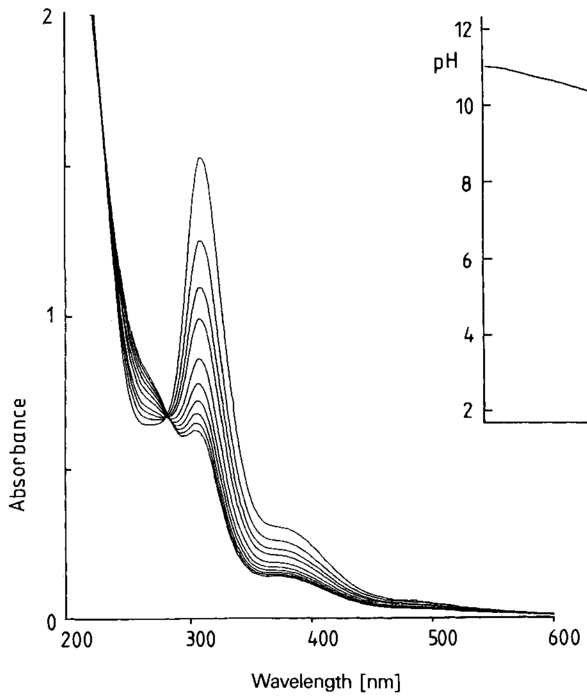


Fig. 1. *The spectrum of* **A** (3 · 10^{-4} M) *in buffered solution* (ph 10), *showing the decrease in absorbance at 310 nm and the appearance of a shoulder at 272 nm due to* **C**. Spectra taken at 2, 7, 12, 17, 27, 37, 47, 57, 67, and 77 min after the addition of **A** to the solution.

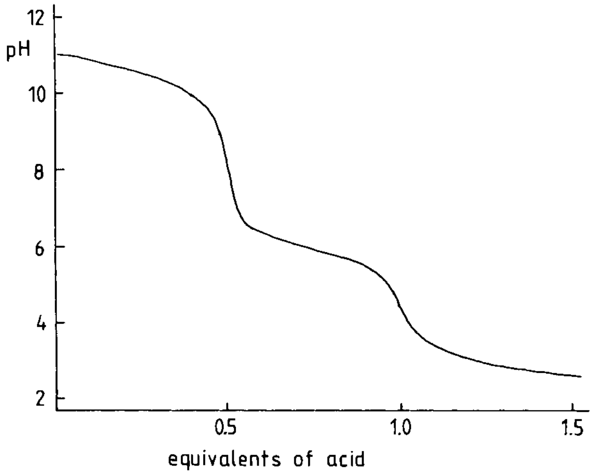


Fig. 2. *Titration curve of a solution of* **A** *with acid after complete decomposition* (0.1 M $NaClO_4$, N_2 purge)

These results are consistent with the following stoichiometry of decomposition:

$$\underset{\mathbf{A}}{2[Co(CN)_5O_2]^{3-}} + H_2O \rightarrow \underset{\mathbf{B}}{[Co(CN)_5(OH)]^{3-}} + \underset{\mathbf{C}}{[Co(CN)_5(OOH)]^{3-}} + O_2 \qquad (3)$$

The hydroperoxide complex **C** has been prepared by reaction of $[Co(CN)_5H]^{3-}$ with O_2 [19] [20] and by protonation of $[(CN)_5CoO_2Co(CN)_5]^{6-}$ [16] [19], and has an absorption band at 272 nm ($\varepsilon = 4400 M^{-1} \cdot cm^{-1}$); the absorbance we observe at 272 nm corresponds to that expected for *Eqn. 3*. The hydroxo complex **B** is quite strongly basic, with an estimated pK_a for $[Co(CN)_5(OH_2)]^{2-}$ of 10.5 [21] [22], very close to the value observed here for the first neutralisation. The second 0.5 equiv. of acid is consumed by the aquation of **C** which is known to be rapid at pH below 7 [19] [23]:

$$\underset{\mathbf{C}}{[Co(CN)_5(OOH)]^{3-}} + H_3O^+ \rightarrow \underset{\mathbf{D}}{[Co(CN)_5(OH_2)]^{2-}} + H_2O_2 \qquad (4)$$

The observed oxidising power of the final solution is accounted for by the liberation of H_2O_2, and the cobalt at the end of the titration will be entirely present as **D**, in agreement with the observed spectrum.

3. *Mechanism of Decomposition of* $[Co(CN)_5O_2]^{3-}$, **A**. The kinetics of the decomposition of **A** does not follow any simple rate law, but qualitative observations of the factors influencing the rate allow us to propose a mechanism for the decomposition. Depending on the conditions of the experiment, the decomposition of **A** can be complete within a few minutes, or only partial after several hours *(Fig. 3)*. The factors we have identified as determining the rate are: a) *The Dioxygen Concentration*. The reaction is accelerated by purging the solution with a current of N_2, and retarded by a current of oxygen when compared to air saturated solutions *(Fig. 3a)*. Under a N_2 purge, the reaction is complete within 20 min at 25° for solutions of **A** in the concentration range 10^{-5}–10^{-3} M. In a closed system, or under an atmosphere of pure O_2, appreciable amounts of **A** may be seen in the spectrum after several hours.

b) *The pH*. The reaction is much faster at low pH *(Fig. 3b)*. For pH values of 8 or less, the hydroperoxo complex **C** is aquated rapidly, and the shoulder at 272 nm is no longer observed. If **A** is dissolved in 0.1M $HClO_4$ the decomposition to **D** is complete within the time necessary to obtain the spectrum.

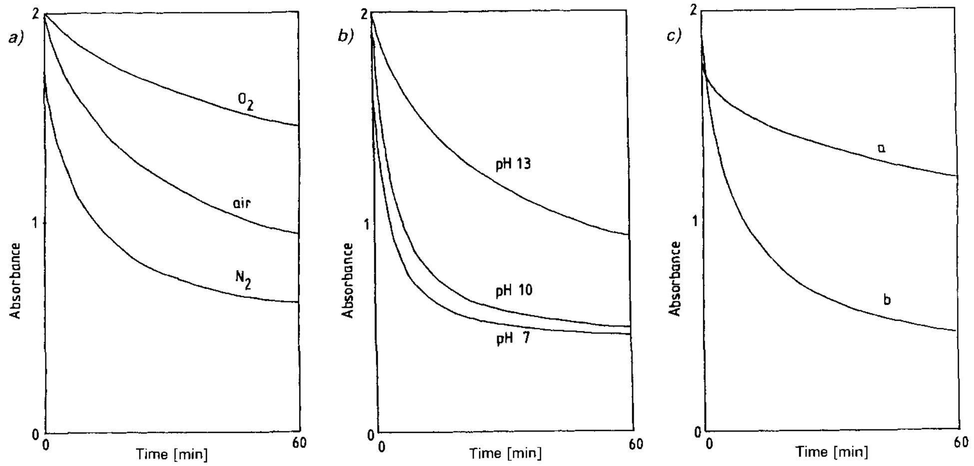


Fig. 3. *The effect on the rate of decomposition of* **A** *as followed by the decrease in absorbance at 310 nm. a)* Decomposition in solutions purged with O_2, air, or N_2 (in 0.1M NaOH). *b)* Decomposition in solutions of 0.1M ionic strength in a current of air at pH 13, 10, and 7. *c)* Decomposition in absence of a gas purge in deionised water *(a)* and in 0.1M $NaClO_4$ *(b)*.

c) *The Ionic Strength*. An increase in the ionic strength considerably accelerates the decomposition *(Fig. 3c)*.

On the basis of these observations, we propose the following mechanism for the decomposition:

$$\underset{\mathbf{A}}{[Co(CN)_5O_2]^{3-}} \rightleftharpoons \underset{\mathbf{E}}{[Co(CN)_5]^{3-}} + O_2 \tag{5}$$

$$\underset{\mathbf{A}}{[Co(CN)_5O_2]^{3-}} + \underset{\mathbf{E}}{[Co(CN)_5]^{3-}} \rightleftharpoons \underset{\mathbf{F}}{[(CN)_5CoO_2Co(CN)_5]^{6-}} \tag{6}$$

$$\underset{\mathbf{F}}{[(CN)_5CoO_2Co(CN)_5]^{6-}} + H^+ \rightleftharpoons \underset{\mathbf{G}}{[(CN)_5Co(OOH)Co(CN)_5]^{5-}} \tag{7}$$

$$\underset{\mathbf{G}}{[(CN)_5Co(OOH)Co(CN)_5]^{5-}} + H_2O \rightarrow \underset{\mathbf{C}}{[Co(CN)_5OOH]^{3-}} + \underset{\mathbf{B}}{[Co(CN)_5OH]^{3-}} + H^+ \tag{8}$$

The kinetics and equilibrium data for *Reactions 5* and *6* have been discussed in some detail by *Fallab* and *Mitchell* [6]. The equilibrium for *Reaction 5* would be expected to lie well to the left, given the strongly reducing character of **E**, but the kinetics are rapid, and **E** can thereby be produced in sufficient quantity to participate in *Reaction 6* – the production of **E** will be favoured by low concentrations of O_2. *Reaction 6*, involving the interaction of two triply charged anions, will be greatly accelerated by high ionic strength as has previously been observed in the kinetics of formation of binuclear peroxo species [24]. *Bayston* and *Winfield* [16] have shown that *Reaction 7* is rapid and reversible, with an estimated pK_a for **G** of 12, but that **G** decomposes rapidly and irreversibly to **B** and **C** *(Reaction 8)*. The effect of the pH is, thus, explained by its influence on the *Equilibrium 7*.

We have observed that, in 4 M KOH solution, a solution of **A** with cobalt concentrations in the range $2 \cdot 10^{-3}$–10^{-2} M decomposes to the dinuclear superoxo complex $[(CN)_5CoO_2Co(CN)_5]^{5-}$ (**H**) identified by its characteristic absorption band at 485 nm [19] [25]. In these conditions, protonation of **F** *(Reaction 7)* is suppressed, and the formation of appreciable quantities of **F** is possible. Complex **F** is quite strongly reducing (the reduction potential of **H** has been reported as – 0.19 V [26]), and may readily be oxidised by the dioxygen produced by *Reaction 5* to give **H** which is appreciably more stable in aqueous solution than **F** [19]. This trapping of **F** by oxidation is further evidence in support of the mechanism. The observation of a reasonable isosbestic point during the decomposition of **A** at lower pH suggests, however, that the concentration of the intermediates is very low in these conditions.

To investigate the possible participation of superoxide anion in the decomposition, we have investigated the effect of the addition of superoxide dismutase to solutions of **A** at neutral pH. No effect on the kinetics of decomposition was observed, and we conclude that superoxide ion is not an intermediate in the mechanism.

The above mechanism is similar to that proposed by *Pignatello* and *Jensen* [27] for the decomposition of $[Co(acacen)O_2(py)]$ in pyridine at – 10° where second-order kinetics in cobalt, and an inverse first-order dependence on oxygen pressure were observed. The authors concluded that there was rapid formation of a binuclear $\eta^1{:}\eta^1$-complex which is then protonated to give $[Co(acacen)(py)]^+$ and H_2O_2.

4. *Reactions with Electron-Transfer Reagents.* To gain further information concerning the reactivity of coordinated dioxygen, we have studied the reactions of **A** with a number of electron-transfer reagents. The general method used was to observe the effect of the reagent on the electronic spectrum, especially the band at 310 nm due to **A** and the band at 272 nm due to **C**, and, whenever possible, the acid-base properties of the final solution. The reactions are complicated by the competition with the decomposition of **A**, and the limited pH range available for study.

4.1. *Oxidising Agents.* 1) *Hexacyanoferrate(III).* The addition of **A** to a solution of hexacyanoferrate(III) results in a drop in intensity of the hexacyanoferrate band at 420 nm and in the band due to **A** at 310 nm, and the band at 272 nm is no longer observed, although the absorption of $[Fe(CN)_6]^{3-}$ at this wavelength interferes with the observation. Titration of the final solution with acid gives a curve qualitatively similar to that in *Fig. 2,* but requires much less acid to complete the neutralisation: if a 1:1 ratio of $[Fe(CN)_6]^{3-}$ to **A** is used, only 40% of the original amount of acid is needed; a fivefold excess of $[Fe(CN)_6]^{3-}$ reduces the amount of acid to 15% of the original value, indicating suppression of the formation of **B** and **C**.

2) *Iodine.* Addition of **A** to solutions of molecular iodine or triiodide anion resulted in lower yields of **B** and **C** as shown by acid titration of the final solution: with a twofold excess of iodine the amount of acid required was only 20% of that required in absence of iodine. The UV part of the spectrum is obscured by the excess of iodine, but in the VIS region the band at 500 nm and the shoulder at 440 nm expected for $[Co(CN)_5I]^{3-}$ were observed.

These reactions may be explained by the trapping of the Co(II) species $[Co(CN)_5]^{3-}$ (**E**) by these two oxidising agents to give the known products $[(CN)_5Co(CN)Fe(CN)_5]^{6-}$ [28] and $[Co(CN)_5I]^{3-}$ [29]. They confirm that the *Equilibrium 5* is indeed rapid, and that **E** may participate in the decomposition mechanism.

4.2. *Reducing Agents.* The reactions of **A** with a variety of reducing agents were investigated to study the oxidising properties of **A**. Since any oxidation reaction of **A** will be in competition with its decomposition, it was necessary to choose conditions in which the decomposition is slow (neutral or alkaline pH), and preferably at a pH > 9 to avoid rapid hydrolysis of the potential reduction product **C**. The general procedure adopted was to add the tetraethylammonium salt of **A** to a buffered solution containing an excess (normally 5:1) of reductant, and to follow the reaction by repetitive scanning of the UV/VIS spectrum of the solution. The results of these observations are summarized in *Table 2.* No attempt was made to isolate the products of the reactions.

Table 2. *Effect of Reducing Agents on the Decomposition of* **A**

Reducing agent	pH	Observation
$S_2O_3^{2-}$	10	No effect
HPO_3^{2-}	10	No effect
SO_3^{2-}	10	Rapid disappearance of **A** and formation of **C**. Slower reaction with **C**
$S_2O_4^{2-}$	10	Identical to sulphite
O_2^{-}	13	Rapid formation of **C**
$[Co(CN)_5]^{3-}$	7	Rapid formation of **C**
L-Cysteine	10	Rapid disappearance of **A**
Hydroquinone	7	Rapid disappearance of **A**, formation of transient brown colour

Two of the reductants studied, thiosulphate and phosphite, had no effect on the decomposition of **A**; in all other cases the disappearance of the absorption at 310 nm was complete within a few minutes, indicating a reaction with **A** which is much faster than the decomposition. Sulphite and dithionite showed essentially identical behaviour, with rapid disappearance of **A**, and a rise in absorbance at 272 nm compatible with the formation of **C**. On standing, a new absorbance at 310 nm gradually appears ($\varepsilon \approx 1400 \text{M}^{-1} \cdot \text{cm}^{-1}$) as a shoulder on the stronger absorption in the UV. We associate this with the product of a second reaction between the sulphur nucleophile and the hydroperoxo complex **C**, as has been observed in our studies of the reactivity of **C** [23].

Although the superoxide anion decomposes in aqueous solution, the rate of this reaction is slow at high pH [30], and it may exist long enough to act as a reducing agent ($E^\circ(O_2/O_2^-) = -0.33$ V [31]). Addition of an excess of KO_2 to a solution of **A** in 0.1M NaOH causes immediate disappearance of the band at 310 nm and a sharp rise in absorption at 272 nm as expected for **C**; the absorbance observed was within 10% of that expected for **C** using $\varepsilon = 4400 \text{M}^{-1} \cdot \text{cm}^{-1}$ reported by *Bayston* and *Winfield* [16]. Titration of the solution obtained from reaction of **A** with KO_2 in the absence of buffer showed over 90% formation of **C** as estimated from the amount of acid required to complete the hydrolysis of **C** (after correction for the neutralisation of the decomposition products of the excess of KO_2).

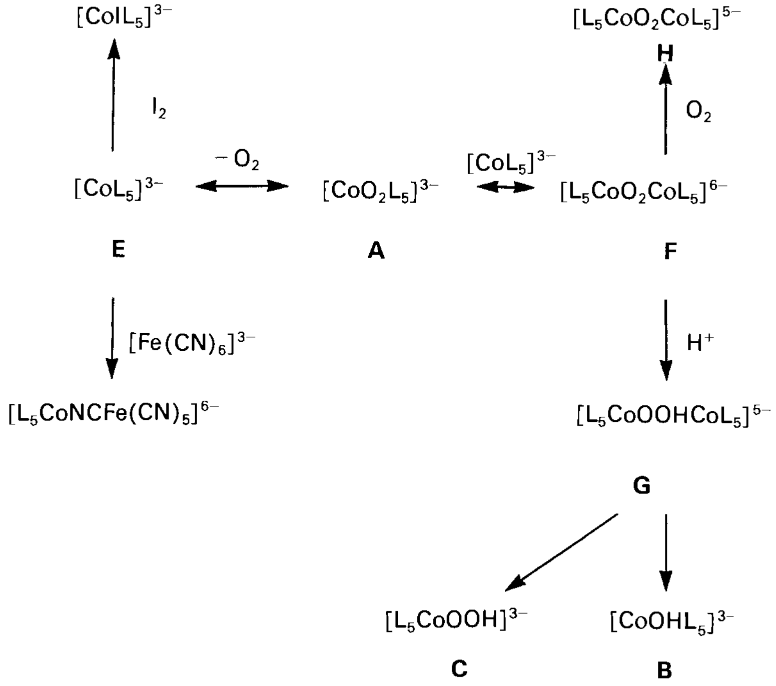
Addition of **A** to a buffered (pH 7) solution of $[Co(CN)_5]^{3-}$ under N_2 showed formation of nearly 1 equiv. of **C** as judged by the absorbance at 272 nm; as expected the **C** formed in this reaction then hydrolyses slowly at this pH. A more quantitative estimate of the extent of reaction was obtained by repeating the experiment in the absence of buffer and titrating the resulting solution with acid. The titration curve indicated the formation of 1.05 equiv. of **B** and 0.95 equiv. of **C**.

Hydroquinone and L-cysteine are potential H-atom donors, and their reaction with **A** was investigated briefly. Hydroquinone (pH 7) reacts within the time of mixing to give a transient brown colour which fades within a few minutes. Strong absorption in the UV prevents the identification of any **C** present. The final spectrum shows a peak at 380 nm whose extinction coefficient is consistent with the quantitative formation of **D**. L-Cysteine (pH 10) also reacts rapidly, and the final solution shows a peak at 380 nm whose intensity ($\varepsilon \approx 2200 \text{M}^{-1} \cdot \text{cm}^{-1}$) is too high for **B** or **D**. A similar peak has been observed on reaction of the hydroperoxo complex **C** with cysteine [23], and it seems reasonable to suppose, therefore, that the initial reaction is the rapid reduction of **A** to **C** by L-cysteine, followed by reaction of **C** with the excess of L-cysteine.

Discussion. – The reactions discussed in this paper are summarised in the *Scheme* which shows the relationships between the different cobalt species. An important feature of this study is the kinetic lability of the dioxygen complexes which results in solutions of the mononuclear η^1-dioxygen complex **A** giving reactions of the dinuclear $\eta^1{:}\eta^1$-dioxygen complex **F** (protonation, oxidation) or of the Co(II) precursor **E** (trapping by oxidants).

The action of the reducing agents studied shows that the mononuclear η^1-dioxygen **A** can be reduced to the hydroperoxo complex **C**. This reaction is clearly an inner-sphere reduction in the case of $[Co(CN)_5]^{3-}$, but is probably an outer-sphere reaction in the case of sulphite and dithionite, since we would expect an O–S bond formed by inner-sphere reduction to be stable enough to allow detection of the intermediate as in the case of reduction of the hydroperoxo complex **C** [23]. The observation of the formation of **C** argues in favour of an outer-sphere mechanism in these two cases. In a study of the reactions of the η^1-dioxygen complex $[Co([14]aneN_4)(OH_2)O_2]^{2+}$. *Kumar* and *Endicott* concluded that both inner-sphere and outer-sphere reduction pathways could be followed [32]. The reduction by superoxide is another potentially outer-sphere process, but it should be noted that **C** could equally be obtained by reaction of the Co(II) precursor **E** with superoxide as previously observed for Co(II) macrocyclic complexes [33] and for superoxide with Fe(II) [34]. The reactions of **A** with hydroquinone and L-cysteine may follow a H radical abstraction mechanism as frequently proposed for η^1-dioxygen species.

Scheme



The results presented here may explain the varied reactivity of $[Co(CN)_5O_2]^{3-}$ with organic substrates as studied by *Nishinaga et al.* Thus, the reaction of **A** with 2,6-di(*tert*-butyl)phenols in the presence of oxygen gave products consistent with the base-catalysed oxygenation of the phenols [11]: both **B** and **F**, produced in the decomposition of **A**, are quite strong bases and could effect this catalysis. With quinones, one- or two-electron reduction was observed [12], which, on the basis of the results presented above, is probably due to the trapping of the highly reducing species **E**. Reaction with stable phenoxy radicals [13] gave mixtures of phenols (presumably resulting from reduction by **E**) and peroxyquinones which would be formed by inner-sphere reduction of **A** by the phenoxy radical. A peroxyquinone-Co(III) complex has indeed been isolated from the reaction of an η^1-dioxygen-cobalt *Schiff* base complex with a phenoxy radical [35]. It, therefore, seems probable that it is only in this final reaction that the η^1-dioxygen species is the active species.

Experimental. – *Source of Compounds.* Tetraethylammonium [dioxygenpentacyanocobaltate(III)] was prepared according to the method of *White et al.* [9] using $CoCl_2$ (previously dried at 140° under vacuum) and Et_4NCN (*Fluka AG*, CH-Buchs) in DMF; yields were typically 70%. Satisfactory elemental analyses (Co, C, H, N) were obtained for each synthesis, assuming a slight variation in the number of molecules of water of crystallisation (varying between 3 and 5). Solutions of pentacyanocobaltate(II) were prepared by dissolving 1 equiv. of $CoCl_2$ and 5 equiv. of KCN in deionised water which was deoxygenated by a vigorous current of N_2. Potassium superoxide (*Ventron* or *Fluka*) was of 95% purity. All other reagents were commercially available and were of highest obtainable purity. DMF was distilled over molecular sieve, and MeCN was dried over P_2O_5. Phosphate (pH 7) and borate (pH 10) buffers were used, with the ionic strength adjusted to 0.1M using $NaClO_4$.

Measurements. UV/VIS spectra were recorded with *Perkin-Elmer Lambda V* or *Kontron Uvikon 820* spectrophotometers with thermostatted cell holders. For experiments under O_2, air, or N_2 atmospheres, solid $(NEt_4)_3[Co(CN)_5O_2] \cdot n\ H_2O$ was added to a magnetically stirred soln. held in a thermostatted polarography cell purged continuously with the desired gas, and the soln. circulated into the spectrophotometer with a peristaltic pump. Unless otherwise stated, all experiments were carried out at 25.0 ± 0.2°. Solns. were typically $3 \cdot 10^{-4}$ M in cobalt. pH Measurements and potentiometric titrations were performed using a *Metrohm E456* potentiograph and automatic burette, and a *EA125* glass microelectrode. The soln. was held in a thermostatted polarographic cell equipped with a magnetic stirrer and which could be purged with a current of gas. The quantity of complex used for titrations was typically $5 \cdot 10^{-5}$ mol, and 0.01M HCl was used for titrations. A *Beckmann Fieldlab* oxygen analyser was used to detect liberation of oxygen. Cobalt analysis was made using atomic-absorption spectroscopy (*Unicam SP-1900*) and C, H, and N analysis carried out by Dr *H. G. Eder* of the University of Geneva, Microanalysis Laboratory.

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