Reduction Potentials for μ-Superoxo/μ-Peroxo-dicobalt(III) Couples

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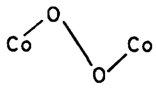
Reduction potentials (*versus* n.h.e.) determined by cyclic voltammetry are reported for 11 μ-superoxo/μ-peroxo-dicobalt(III) couples. A dependence of $E^\ominus$ values on the identity of bridging and terminal ligands, and on the degree of chelation of amines is observed. The effect of protonation of μ-peroxo ligands on $E^\ominus$ values at pH < 3 is noted.

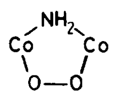
Although Co^{II} has no known function as a biological oxygen carrier, the readiness with which it combines with O_2 to form adducts and the chemistry of the products so formed is of continuing interest.[1–5] Depending on the ligands used and conditions adopted 1 : 1 and/or 2 : 1 (Co : O_2) products can be isolated.[6] The 2 : 1 adducts, of which (A)—(C) are examples, are referred to as μ-peroxo-dicobalt(III) complexes. Structure types (A)—(C) provide the subject of the present study. Upon 1 : 1 oxidation μ-superoxo-dicobalt(III) complexes are formed, where the preparative details and characterisation of products are well established.[7] As yet no systematic study of the thermodynamics of interconversion of μ-superoxo and μ-peroxo complexes in terms of reduction potentials, $E^\ominus$ values (*versus* n.h.e.), has been reported, in a number of cases because one or other of the complexes is unstable as the pH is varied. The use of cyclic voltammetry provides a means of obtaining such information.

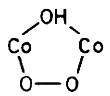
Experimental

Complexes as listed in Table 1 were prepared by established procedures, and their authenticity checked by reference to published u.v.-visible spectra.[7–15] Solutions of complexes (20 cm^3, 1—2 mM) were made up, and the $[H^+]$ adjusted to required values with dilute perchloric acid (B.D.H., AnalaR). Ionic strengths were maintained at 0.245 M (or as stated) with sodium perchlorate (B.D.H., AnalaR). For the μ-amido-μ-superoxo complexes with 1,10-phenanthroline and 2,2′-bipyridine respectively as ligands, nitric acid/sodium nitrate (both B.D.H., AnalaR) were used because of the low solubility of perchlorate salts.

Reduction potentials were determined by cyclic voltammetry employing a conventional three-electrode cell containing platinum working and counter electrodes, and a Radiometer (K401) saturated ($Hg–HgCl_2–KCl$) calomel electrode. The cell was thermostatted at 25 °C using a double-walled vessel through which thermostatted water was circulated. The cell temperature was monitored (±0.1 °C) with a Comark model 3007 digital thermometer. Solutions were deoxygenated using an N_2 gas stream prior to cyclic experiments. Response curves were generated with a Chemical Electronics (Birtley Co. Durham) model DD50SU Potentiostat. The output voltage was followed with a Data Precision DMM1 high impedence voltmeter, and plotted on a J. J. Lloyd PL51 X-Y chart recorder. Measured reduction potentials, $E_{obs.}$ were taken as the mean value of the anodic (E_a) and cathodic (E_c) peaks observed in voltammograms at a given scan rate. Scan rates used varied from 0.3 V s^{-1} for the $[(NH_3)_5Co(\mu\text{-}O_2)Co(NH_3)_5]^{5+,4+}$ study to 0.01 V s^{-1} used in most other cases, which was slow enough to allow the isomerisation reaction as applicable to the $[(en)_2Co(\mu\text{-}NH_2,O_2)Co(en)_2]^{4+,3+}$ (and possibly other systems) to occur. All reduction potentials quoted are with reference to the normal hydrogen electrode (n.h.e.) at 25 °C. The saturated calomel electrode was assumed to have a potential of 0.244 V. Values of $E_{obs.}$ are the average of at least two determinations. Errors were estimated to be ±2 mV. Formal $E^\ominus$ values for the conditions specified were obtained after due allowance for $[H^+]$ effects as described in the Results section.


(A)


(B)


(C)

Reduction potentials were checked in one case by potentiometry when solutions containing known amounts of both μ-superoxo and μ-peroxo complexes were made up. The resulting potential was measured, using a voltmeter attached to platinum and calomel electrodes, after the reading had stabilised (*ca.* 5 min). Values of $E_{obs.}$ were calculated using the Nernst equation. Good agreement (±2 mV) was obtained in the case of the $[(en)_2Co(\mu\text{-}NH_2,O_2)Co(en)_2]^{4+,3+}$ couple.

Results

For cyclic voltammetry studies either the μ-superoxo or μ-peroxo form was selected as starting complex (see Table 2), according to ease of preparation and/or stability in solution. Some μ-peroxo complexes are known to exhibit instability in the more acidic solutions,[16] whereas μ-superoxo complexes are generally unstable under neutral or basic conditions.[17,†] Extremes of this behaviour are observed with the $[(NH_3)_5Co(\mu\text{-}O_2)Co(NH_3)_5]^{5+,4+}$ complexes, where the μ-superoxo 5+ form is unstable at pH > 3, and the μ-peroxo complex for most conditions <8 M in NH_3. Decay processes are rapid and can occur within periods of *ca.* 1 min. As a result measurements of this $E^\ominus$ have proved particularly difficult. A recent study has indicated that at pH < 2 protonation of the μ-peroxo ligand in fact stabilises the complex to intramolecular charge-transfer decomposition,[16] and this stabilisation is further enhanced by the presence of Cl^- (>0.6 M). Accordingly meaningful measurements have been possible for the conditions $[H^+]$ in the range 0.1—2.0 M, $[Cl^-] = 2.0$ M, and $I = 2.0$ M(NaCl). Evidence has been obtained previously [$I = 2.3$ M(NaCl)] for protonation of the μ-peroxo complex, protonation constant $K_1 = 11.9\ M^{-1}$ at 25 °C;[16] this form does not convert to the μ-superoxo complex. Here a linear plot of slope 0.059 (one-electron process with $n = 1$) was obtained with $K_1 = 10.1 \pm 0.5\ M^{-1}$, consistent with equation (1).

Non-S.I. units employed: M = mol l^{-1}.

† See comments under ref. 4 of ref. 15.

Table 1. Details of literature u.v.–visible absorption spectra used in characterisation of complexes *

(*a*) μ-Peroxo complexes	λ/nm (ε/M^{-1} cm^{-1})	λ/nm (ε/M^{-1} cm^{-1})	Reference
$[(en)(dien)Co(\mu\text{-}O_2)Co(dien)(en)](ClO_4)_4\cdot 2H_2O$	420 (557)		8
$[(NH_3)(trien)Co(\mu\text{-}O_2)Co(trien)(NH_3)](ClO_4)_4\cdot 2H_2O$	562 (230)		8
$K_6[(CN)_5Co(\mu\text{-}O_2)Co(CN)_5]$	310 (1.0 × 10^4)	370 (5.0 × 10^3)	9
$[(tren)Co(\mu\text{-}NH_2,O_2)Co(tren)](ClO_4)_3\cdot H_2O$	325 (5.0 × 10^3)	484 (576)	10
$[(en)_2Co(\mu\text{-}OH,O_2)Co(en)_2](ClO_4)_3\cdot H_2O$	355 (5.38 × 10^3)		11
$[(trien)Co(\mu\text{-}OH,O_2)Co(trien)](ClO_4)_3$	355 (4.7 × 10^3)		12
(*b*) μ-Superoxo complexes			
$[(NH_3)_5Co(\mu\text{-}O_2)Co(NH_3)_5](ClO_4)_5\cdot 2H_2O$	297 (2.45 × 10^4)	670 (890)	7
$K_5[(CN)_5Co(\mu\text{-}O_2)Co(CN)_5]\cdot H_2O$	310 (1.73 × 10^4)	485 (1.1 × 10^3)	9, 13
$[(NH_3)_4Co(\mu\text{-}NH_2,O_2)Co(NH_3)_4](NO_3)_4$		700 (306)	7
$[(en)_2Co(\mu\text{-}NH_2,O_2)Co(en)_2](NO_3)_4\cdot 2H_2O$		687 (485)	7
$[(phen)_2Co(\mu\text{-}NH_2,O_2)Co(phen)_2](ClO_4)_4\cdot 2H_2O$	482 (1 080)	700 (506)	14, 15
$[(bipy)_2Co(\mu\text{-}NH_2,O_2)Co(bipy)_2](ClO_4)_4\cdot H_2O$	475 (934)	695 (440)	14, 15

* en = $NH_2CH_2CH_2NH_2$; trien = $NH_2CH_2CH_2(NHCH_2CH_2)_2NH_2$; phen = 1,10-phenanthroline; dien = $NH_2CH_2CH_2NHCH_2CH_2NH_2$; tren = $N(CH_2CH_2NH_2)_3$; and bipy = 2,2′-bipyridine.

Table 2. Reduction potentials $E^\ominus$ (*versus* n.h.e.) for μ-superoxo/μ-peroxo-dicobalt complex at 25 °C, $I = 0.45$ M ($NaClO_4$), $[H^+] = 2.0 \times 10^{-3}$ M, using cyclic voltammetry, scan rates 0.01—0.30 V s^{-1}. Starting complex (*ca.* 1—2 mM) is indicated by S (superoxo) or P (peroxo). Categories (A)—(C) indicate the single bridged, the μ-amido, and μ-hydroxo series of complexes respectively

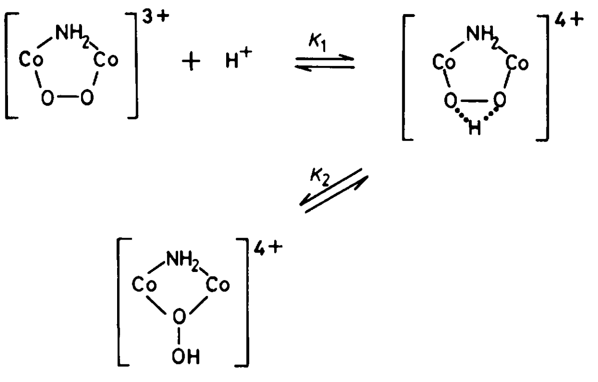
	Complex	$E^\ominus$ (V)	Effect of H$^+$	
(A)	$[(NH_3)_5Co(\mu\text{-}O_2)Co(NH_3)_5]^{5+}$	0.713(S) [a]	Dependence	pH <1.0
	$[(en)(dien)Co(\mu\text{-}O_2)Co(dien)(en)]^{5+}$	0.905(P)	No dependence	pH 2.7—6.4
	$[(NH_3)(trien)Co(\mu\text{-}O_2)Co(trien)(NH_3)]^{5+}$	0.911(P) [b]		
	$[(CN)_5Co(\mu\text{-}O_2)Co(CN)_5]^{5-}$	−0.194(S) [b]		
(B)	$[(NH_3)_4Co(\mu\text{-}NH_2,O_2)Co(NH_3)_4]^{4+}$	0.780(S)		
	$[(en)_2Co(\mu\text{-}NH_2,O_2)Co(en)_2]^{4+}$	0.863(S)	Dependence	pH 0.6—2.7
	$[(tren)Co(\mu\text{-}NH_2,O_2)Co(tren)]^{4+}$	0.962(P)	Dependence	pH 0.6—3.0
	$[(phen)_2Co(\mu\text{-}NH_2,O_2)Co(phen)_2]^{4+}$	1.156(S) [c]	No dependence	pH 0.6—3.0
	$[(bipy)_2Co(\mu\text{-}NH_2,O_2)Co(bipy)_2]^{4+}$	1.159(S) [c]		
(C)	$[(en)_2Co(\mu\text{-}OH,O_2)Co(en)_2]^{4+}$	0.930(P)		
	$[(trien)Co(\mu\text{-}OH,O_2)(trien)]^{4+}$	1.055(P)		

[a] $I = 2.00$ M (NaCl). [b] $[H^+] = 1.0 \times 10^{-3}$ M. [c] $I = 0.245$ M ($NaNO_3$).

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

Hence K_1 is in good agreement with the previous value and from the intercept an $E^\ominus$ value of 0.713 V is obtained for the condition with no μ-peroxo complex inactivated by protonation. McLendon and Mooney [18] have reported earlier attempts to determine $E^\ominus$ from cyclic voltammetry (~0.90 V) and potentiometry (0.95 V). However details of their procedure, and indeed feasibility of their approach in view of the above restrictions, remain far from clear. The $E^\ominus$ which McLendon and Mooney [18] obtained for the $[(NH_3)_4Co(\mu\text{-}NH_2,O_2)Co(NH_3)_4]^{4+,3+}$ couple (0.75 V) is on the other hand in excellent agreement with the value reported here (0.78 V). The third measurement which they report for the $[(CN)_5Co(\mu\text{-}O_2)Co(CN)_5]^{5-,6-}$ couple differs by some 0.25 V from the value reported in Table 2.*

Cyclic experiments on the $[(en)(dien)Co(\mu\text{-}O_2)Co(dien)(en)]^{4+}$ complex at pH 6.4 have indicated that the μ-superoxo 5+ complex undergoes decomposition when a slow scan rate is used (0.003 V s^{-1}) but not with a high scan rate (0.30 V s^{-1}). The $E^\ominus$ obtained is independent of pH over the range 2.7—6.4.



(D)

(2)

The variation of $E^\ominus$ with pH in the range 0.6—3.0 was investigated for three ($\mu\text{-}NH_2,O_2$) complexes, series (B) in Table 2. Results are illustrated in the Figure. Previous studies have provided evidence for protonation of μ-peroxo but not μ-superoxo complexes,[2] and all observations in connection with the present work support this belief. Protonation and isomerisation as in (2) have been established for the μ-peroxo ethylenediamine complex, $[(en)_2Co(\mu\text{-}NH_2,O_2)Co(en)_2]^{3+}$. Hence the relationship (3) can be derived.

$$E_{\text{obs.}} = E^\ominus + \frac{0.059}{n}\log\{1 + K_1(1 + K_2)[H^+]\} \qquad (3)$$

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* The error (±10 mV) in the measurement of this $E^\ominus$ is bigger than for other $E^\ominus$ values reported herein, and some difficulty was experienced in obtaining satisfactory reversibility in voltammograms at other pH's.

Using known values of the protonation constant K_1 (6.95 M^{-1}) and K_2 (1.1) at 25 °C, $I = 0.245$ M,[19] a linear plot of $E_{obs.}$ (seven values in the range 0.863—0.887) against $\{1 + K_1(1 + K_2)[H^+]\}$ is obtained. The slope of 0.059 is consistent with a one-electron change. The intercept gives $E^{\ominus} = 0.863$ V. It should be noted here that $K_1(1 + K_2)$ in (3) replaces the K_1 term in equation (1). No evidence was obtained previously[16] for the isomerisation step K_2 in studies on the $[(NH_3)_5Co(\mu\text{-}O_2)Co(NH_3)_5]^{4+}$ complex. If such a step is at any time identified then K_1 will have to be adjusted accordingly, and equation (3) will become relevant instead of (1). Similarly for the $[(tren)Co(\mu\text{-}NH_2,O_2)Co(tren)]^{4+,3+}$ couple K_1 or $K_1(1 + K_2)$ $= 7.1 \pm 0.5$ M^{-1} and linear plots of slope 0.059 are obtained.

The two (μ-OH,O_2) complexes were studied at pH = 2.7 only. At lower pH's hydroxo-bridge cleavage is known to occur.[12] In these and other instances it was assumed that pH of 2.7 did not give rise to protonation.

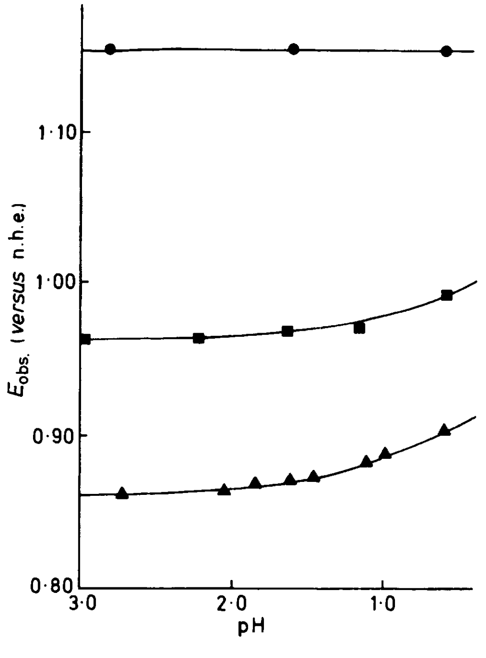

Figure. The variation of $E_{obs.}$ (25 °C) with pH at $I = 0.245$ M ($NaClO_4$) for the (μ-NH_2,O_2) couples $[(en)_2Co(\mu\text{-}NH_2,O_2)Co(en)_2]^{4+,3+}$ (▲); $[(tren)Co(\mu\text{-}NH_2,O_2)Co(tren)]^{4+,3+}$ (■); and $[(phen)_2Co(\mu\text{-}NH_2,O_2)Co(phen)_2]^{4+,3+}$ (●)

Discussion

Reduction potentials $E^{\ominus}$, Table 2, for the (μ-O_2^-)–(μ-O_2^{2-}) couples exhibit considerable variation as the identity of the terminal ligands is varied. For the (μ-NH_2,O_2) complexes [series (B)] $E^{\ominus}$ values give a 0.38 V variation for ligands investigated, which is strikingly similar to the variation observed for the mononuclear Co^{III}–Co^{II} couples with the same ligands: $[Co(phen)_3]^{3+/2+}$ (0.37),[20] $[Co(bipy)_3]^{3+,2+}$ (0.37),[21] $[Co(en)_3]^{3+,2+}$ (0.18),[22] and $[Co(NH_3)_6]^{3+,2+}$ (~0.108 V).[23] The trend is moreover continued on inclusion of the value for the $[(CN)_5Co(\mu\text{-}O_2)Co(CN)_5]^{5-,6-}$ couple (−0.194 V) since $[Co(CN)_5(H_2O)]^{2-}$ is reported to have a negative reduction potential (−0.43 V).[24] A second effect to note is the apparent increase in $E^{\ominus}$ values as the degree of chelation of amine ligands increases [first three entries under (B) in Table 2]. Thirdly bridging ligands are also influential as can be seen by comparing $E^{\ominus}$ for the ethylenediamine complexes (μ-NH_2,O_2) (0.863 V) and (μ-OH,O_2) (0.930 V). Different degrees of ring strain stemming from optimisation of Co–N–Co and Co–O–Co bond angles is no doubt a contributing factor. A comparison of the $E^{\ominus}$ values for $[(NH_3)_5Co(\mu\text{-}O_2)Co(NH_3)_5]^{5+,4+}$ ($E^{\ominus}$ 0.713 V) and $[(NH_3)_4Co(\mu\text{-}NH_2,O_2)Co(NH_3)_4]^{4+,3+}$ ($E^{\ominus}$ 0.780 V) suggests a dependence on orientation of the O_2 bridge which is *trans* for (A)[25] and *cis* for (B).[26]

It is possible to rationalise the effects of terminal ligands in so far as the 1,10-phenanthroline and 2,2′-bipyridine ligands (*via* the Co metal atom) induce electron withdrawal from the O_2^{2-} bridge, thus stabilising the bridge to oxidation. With cyanide as ligand on the other hand the negative charge will tend to push more charge onto the peroxo bridge. If these trends are dominant then they would be expected to be supported by different degrees of protonation of the μ-peroxo ligand. The position with regard to the cyano-μ-peroxo complex does not appear to have been clearly established. However protonation of the (μ-NH_2,O_2) complexes is seen to become more significant for the ligands phen < tren < en, see Figure. Although no effect of protonation of the μ-peroxo phenanthroline complex was noted in the range pH 0.6—3.0, a significant change of u.v.–visible spectrum has been reported on addition of 8 M acid.[15] Protonation of the ethylenediamine complex appears to have two consequences. First rapid protonation is followed by isomerisation to (D) as in equation (2).[19] At present the ethylenediamine complex with the μ-peroxo ligand co-ordinated as in (D) is the only example of this kind to have become firmly established (with confirmation from *X*-ray crystallography),[27] although it would be surprising if analogous structures did not exist in other cases and in particular for the complex $[(NH_3)_4Co(\mu\text{-}NH_2,O_2)Co(NH_3)_4]^{3+}$. The second consequence of protonation and a relatively small $E^{\ominus}$ value is that disproportionation of the μ-peroxo complex to μ-superoxo and μ-hydroxo states can in some cases occur.[28] The existence of (D) with its smaller four-membered central ring system appears to be an essential feature making such a reaction possible. It provides, incidentally, possibly the most facile route to O–O cleavage in this chemistry. Maeder and Fallab[29] have recently established a second case of disproportionation with the single-bridged glycine (gly) μ-peroxo complex $[(gly)(dien)Co(\mu\text{-}O_2)Co(dien)(gly)]^{2+}$. The μ-superoxo product has been identified. Of prime interest is the $E^{\ominus}$ value of 0.693 V at pH 1, $I = 0.245$ M ($NaClO_4$).[30] A dependence of $E^{\ominus}$ on pH is apparent at pH < 1.5, and a protonation constant K_1 = *ca.* 10 M^{-1} is observed. Although there is at present no direct evidence for structure (D) it would be surprising if this were not formed in the circumstances. No disproportionation of $[(NH_3)_5Co(\mu\text{-}O_2)Co(NH_3)_5]^{4+}$ has yet been detected.

Finally the present study, in so far as it provides information on the chemistry of μ-peroxo forms generally, is of interest in the wider context of biological oxygen carriers.[31] Of the three known carriers hemocyanin and hemerythrin have binuclear metal active sites consisting of $2Cu^I$ and $2Fe^{II}$'s respectively. Oxy forms are formulated as $Cu^{II}{}_2O_2{}^{2-}$ and $Fe^{III}{}_2O_2{}^{2-}$ respectively, where although no *X*-ray crystal structure information on the O_2-carrying forms is yet available there is some evidence from EXAFS (extended *X*-ray absorption fine structure) studies for μ-peroxo bridged co-ordination.[32,33] Endogenous bridging ligands are also present in both these cases.[34] Clearly the μ-peroxo-dicobalt(III) complexes and the influence which various factors have on stability provide one possible means of assessing and understanding the relevant active-site chemistry.

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