Cobalt Complexes of Ethylenediamine-N,N'-diacetic Acid and Ethylenediamine-N,N-diacetic Acid: Two-Nitrogen Oxygen Carriers[1a]

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Reactions of molecular oxygen with cobalt complexes of ethylenediamine-N,N'-diacetic acid (SEDDA) and ethylenediamine-N,N-diacetic acid (UEDDA) are described. The equilibrium constants (K_{O_2} = [MLO$_2$OHML][H$^+$]/[ML]^2[O$_2$]) for the oxygenation reaction are reported as K_{O_2} = $10^{-4.24}$ M^{-1} and $10^{-5.3}$ M^{-1} for SEDDA and UEDDA, respectively. Kinetic constants for the oxygenation reaction ML + O$_2$ → MLO$_2$ (k_1) are k_1 = 25 M^{-1} sec^{-1} (SEDDA) and 22 M^{-1} sec^{-1} (UEDDA). The relationship between these experimental constants, the electronic structure of the complexes, and the significance of the results in light of earlier investigations are discussed.

Introduction

The interaction of molecular oxygen with cobalt(II) complexes has recently generated considerable interest as a model for biological systems.[2-4] However, the properties of these complexes which determine the nature of this binding, particularly with regard to the important properties of reversibility and stability, are not yet well understood. We have recently delineated the nature of reversible complexes which are very stable, undergoing no measurable irreversible oxidation to Co(III), based on the use of the isomeric diethylenetriaminemonoacetic acids (DTMA) as ligands.[5] We here report the complexation of molecular oxygen by Co(II) complexes incorporating the isomeric ethylenediaminediacetic acids (symmetrical EDDA and unsymmetrical EDDA), the diacetic acid analogs of DTMA, in an attempt to define more closely the salient requirements for complexation of molecular oxygen, reversibility, and stability toward irreversible oxidation.

It has been previously assumed[6-8] that at least three nitrogens must be present in the coordination sphere of cobalt to allow oxygen complexation. The results presented herein refute this idea thus further defining the constitutional requirements for oxygen adduct formation.

Experimental Section

Chemicals. *N*-Acetylethylenediamine. Ethyl acetate (176 g, 2 mol) and ethylenediamine (240 g, 4 mol) were mixed and refluxed for 20 hr. The reaction mixture was concentrated using a rotary evaporator and the residual liquid was distilled in vacuo; yield 100 g (49%); bp 115° (0.3 Torr). (The residue is mostly *N,N'*-diacetylethylenediamine which can be handsomely crystallized from 95% ethanol.)

Ethylenediamine-*N,N*-diacetic Acid (UEDDA). *N*-Acetylethylenediamine (10.2 g, 0.1 mol) was dissolved in 15 ml of water and bromoacetic acid (27.8 g) in 25 ml of water. The two solutions were combined with 25 ml of water, and, with the temperature maintained at 35°, NaOH (16 g, 0.4 mol) solution in 50 ml of water was added dropwise over 1 hr. The protecting acetyl group was removed by saponification after addition of 50 ml of 5 *M* sodium hydroxide and allowing the mixture to stand overnight. The solution was neutralized to pH 4 with a 20% hydrochloric acid solution. The volume was adjusted to 300 ml with water and the resulting solution was treated with 600 ml of absolute ethanol to precipitate the compound as an oily solid after decantation; the residue was redissolved in water and reprecipitated with ethanol as a solid material; yield 12.3 g (70%).

Ethylenediamine-*N,N'*-diacetic acid (SEDDA) was purchased from K&K Laboratories. Both SEDDA and UEDDA were recrystallized from a minimum of hot water and checked for purity by potentiometric titration (UEDDA mol weight calcd 176, found 177).

Cobalt solutions were prepared from cobalt(II) nitrate and standardized by EDTA titration.

Potentiometric Measurements. All potentiometric measurements were performed in a jacketed titration cell thermostated at 25.0 ± 0.1°. Ionic strength was maintained at 0.10 (KNO$_3$). Measurements were made with a Beckman Research Model pH meter fitted with standard glass and calomel electrodes. The meter was standardized with acid solution (HCl or acetic acid) so that H$^+$ concentration rather than activity was measured.

Equilibria involving ligand only or the interactions of metal and ligand in their various protonated forms were studied under argon atmosphere scrubbed of O$_2$ by passage through Co(CN)$_5$ or SnCl$_2$ solution. Oxygenation equilibria were studied under pure oxygen (p_{O_2} = 1.0 atm) or air (p_{O_2} ≃ 0.2 atm) which had been scrubbed of CO$_2$ by passage through Ascarite.

The data were analyzed by the simultaneous solution of the appropriate mass balance and charge balance equations, assuming the simplest model consistent with and resulting in a good description of the data. Details of these procedures can be found in standard references.[11] Calculations were performed on a high-speed computer (IBM 360/65).

Oxygen Uptake. Oxygen uptake experiments were performed at 25° using a polarographic oxygen sensor (Yellow Springs Instrument Co.). The sensor was calibrated with air-saturated and oxygen-saturated water before each determination.

In a typical determination, an oxygen-saturated low-pH solution of a Co^{II}–EDDA complex of known concentration was placed in the cell and the initial oxygen concentration determined. A very small aliquot of strong base was added to raise the pH and allow complex formation. On attaining equilibrium, the equilibrium oxygen concentration was determined. From the oxygen consumption, the amount of oxygen complex formed could be determined, and an equilibrium constant could be computed by applying the appropriate mass balance expressions.

Kinetics. Kinetics experiments were performed on a Durrum-Gibson D-150 stopped-flow spectrophotometer, following the appearance or disappearance of the 360-nm absorption band characteristic of the oxygen complex. pH was controlled using borate buffers. In all kinetic experiments, the concentration of the Co^{II}–EDDA complex was in at least tenfold excess of oxygen and excellent pseudo-first-order kinetics were observed. Data were analyzed assuming the mechanism proposed by Wilkins.[7,8,10]

Spectra. Spectra were taken on either a Pye–Unicam or a Cary 14 spectrophotometer. Conditions for obtaining extinction coefficients were chosen such that complex formation was essentially complete. The absorbance at λ 360 nm was utilized to obtain an external check on the validity of the oxygenation equilibrium constant, by obtaining spectra at various pH's, calculating the concentration of oxygen complex from its absorbance at λ 360 nm, and partitioning the remaining analytical concentrations of metal and ligand according to their relevant equilibrium constants. The value of log k_{O_2} obtained in this way is in good agreement with the potentiometric and O$_2$ uptake values.

Results

Spectra. On exposing an alkaline (pH >10) solution of Co^{II}SEDDA or Co^{II}UEDDA to oxygen, an intense brownish green color develops, with the solution exhibiting a strong absorption band at ca. 360 nm (Table I). This band is of about the same energy and intensity as those ubiquitously found in μ-peroxo-bridged systems[2a] (e.g., (tren)CoO$_2$OHCo(tren), λ$_{max}$ 350 nm, ε 3860[12]) and is attributed to a M → L charge transfer. No such band is found in spectra of Co^{II}–EDDA solutions prepared under strict anaerobic conditions nor in the spectrum of the red decomposition products which develop after a period of days and are no longer capable of interacting with oxygen (these red products are almost certainly irreversibly

Table I. Electronic Spectra Maxima of Co–EDDA Complexes in the Presence and Absence of Oxygen at High pH

Complex	λ_{max}, nm	ϵ_{max}	Complex	λ_{max}, nm	ϵ_{max}
Co(SEDDA)O$_2$	360	~3300	Co^{III}-SEDDA^a	560	180
Co(UEDDA)O$_2$	362	~3150	Co^{III}-UEDDA^c	550	100

^{a} Decomposition products.

Table II. Special Characteristics of Dibridged μ-Peroxo-μ-hydroxo and Monobridged μ-Peroxo Complexes^a

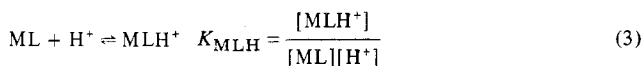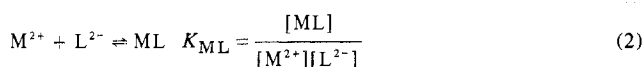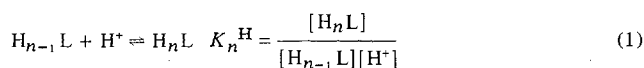| Complex	λ_{max}, nm	Ref
(SEDDA)CoO$_2$(OH)Co(SEDDA)	360	This work
(UEDDA)CoO$_2$(OH)Co(UEDDA)	362	This work
Co(en)$_2$O$_2$(OH)Co(en)$_2$	340	13
(tren)CoO$_2$(OH)Co(tren)	350	12, 14
(histam)CoO$_2$(OH)Co(histam)	375	13
(SDTMA)CoO$_2$(OH)Co(SDTMA)	350	5
(NH$_3$)(tren)CoO$_2$Co(tren)NH$_3$	303, 380 sh^b	12, 14
(L-hist)$_2$CoO$_2$Co(L-hist)$_2$	320, 380 sh	13
(L-DAP)$_2$CoO$_2$Co(L-DAP)$_2$	375, 380 sh	13

^{a} Abbreviations: tren, tris(aminoethyl)amine; SEDDA, ethylenediamine-N,N'-diacetic acid; UEDDA, ethylenediamine-N,N-diacetic acid; L-hist, L-histidine; L-DAP, L-1,2-diaminopropane; histam, histamine; SDTMA, N,N-bis(2-aminoethyl)glycine. ^{b} sh = shoulder.

oxidized Co(III) complexes). It is of some interest that the band occurs at a wavelength more typical of dibridged complexes (μ-peroxo-μ-hydroxo) than singly bridged μ-peroxo systems, which generally absorb at somewhat higher energies[12,13] and show two bands, a high-energy band at ~300–320 and a lower energy shoulder at ~380 nm, while the dibridged complexes show only one strong absorption maximum at 350–360 nm. (See Table II.) This offers further support for our assignment of a dibridged nature for the complex.

Potentiometric Data. Potentiometric titration curves for SEDDA (L), the Co(II) complex formed under inert atmosphere (Ar), and the oxygen complex formed under oxygen atmosphere (O₂) are given in Figure 1. Similar curves for UEDDA are presented in Figure 2. In both cases the ligand curve shows a sharp break at a = 1, corresponding to the titration of the first proton. The chelate curves exhibit a sharp break at a = 2 under nitrogen atmosphere.

In Figure 2, the UEDDA–Co^{II} system under oxygen exhibits a small inflection at a = 2.5 indicating formation of binuclear species. Such an inflection may be masked in the SEDDA system by the buffering properties of high-ph solutions. The oxygen curves are depressed below the titration curves obtained under nitrogen atmosphere indicating increased stability of the oxygen complex.

Equilibrium constants for protonation of the ligand, chelate formation, chelate protonation, chelate hydrolysis, and oxygen complex formation as defined in eq 1–5 were calculated from the potentiometric data and are presented in Table III.

$$H_{n-1}L + H^+ \rightleftharpoons H_nL \quad K_n^H = \frac{[H_nL]}{[H_{n-1}L][H^+]} \quad (1)$$

$$M^{2+} + L^{2-} \rightleftharpoons ML \quad K_{ML} = \frac{[ML]}{[M^{2+}][L^{2-}]} \quad (2)$$

$$ML + H^+ \rightleftharpoons MLH^+ \quad K_{MLH} = \frac{[MLH^+]}{[ML][H^+]} \quad (3)$$

$$MLOH^- + H^+ \rightleftharpoons ML \quad K_{MLOH} = \frac{[ML]}{[MLOH^-][H^+]} \quad (4)$$

$$2ML + O_2 \rightleftharpoons M_2L_2O_2OH + H^+ \quad K_{O_2} = \frac{[M_2L_2O_2OH^-][H^+]}{[ML]^2[O_2]} \quad (5)$$
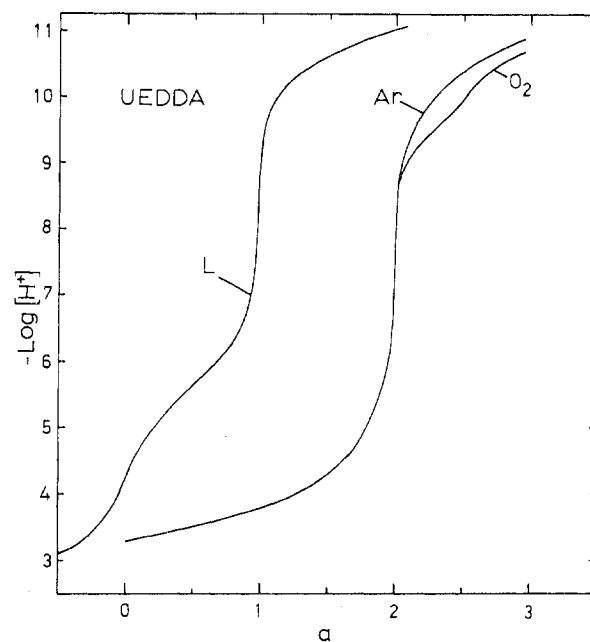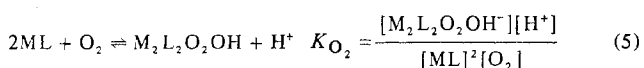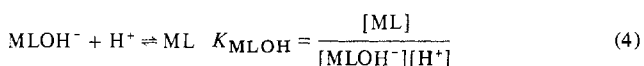
Figure I. Potentiometric equilibrium curves for the Co^{II}-SEDDA-O$_2$ system; ionic strength μ = 0.1 M (KNO$_3$), T = 25°: L, ligand only; Ar, 1:2 molar ratio of cobalt(II) to ligand under an inert atmosphere; O$_2$, 1:1 molar ratio of cobalt(II) to ligand under an oxygen atmosphere; a = moles of base (KOH) added per mole of ligand present.
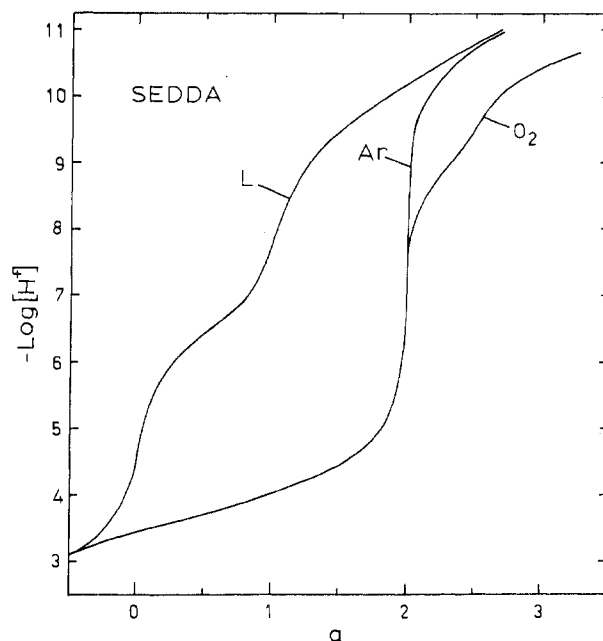
Figure 2. Potentiometric equilibrium curves of the Co^{II}-UEDDA-O$_2$ system; ionic strength μ = 0.1 M (KNO$_3$), T = 25°: L, ligand only; Ar, 1:1 molar ratio of cobalt(II) to ligand under an inert atmosphere; O$_2$, 1:1 molar ratio of cobalt(II) to ligand under an oxygen atmosphere; a = moles of base (KOH) added per mole of ligand present.

Table III. Equilibrium Constants

	SEDDA	UEDDA		SEDDA	UEDDA
$\log K_1^H$	9.63 ± 0.03	11.13 ± 0.02	$\log K_{MLH}$	4.20 ± 0.02	4.95 ± 0.02
$\log K_2^H$	6.55 ± 0.03	5.65 ± 0.02	$\log K_{MLOH}$	10.60 ± 0.02	10.75 ± 0.02
$\log K_{ML}$	11.20 ± 0.02	11.59 ± 0.04	$\log K_{O_2}$	−4.24 ± 0.06	−5.3 ± 0.1

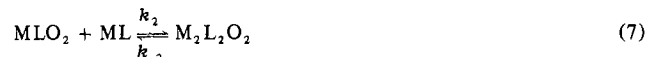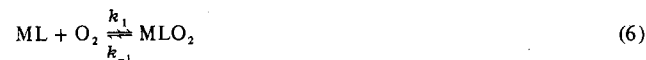**Table IV.** Kinetic Parameters for CoEDDA, $(25°)^a$

	k_1, M^{-1} sec^{-1}	k_{-2}, sec^{-1}
CoUEDDA	22	4.14
CoSEDDA	25	10.4

^{a} k_1 and k_1 defined by eq 6 and 7.

Oxygenation equilibria were studied potentiometrically utilizing both forward (with KOH) and reverse titration (with HCl). Regardless of which direction was chosen to approach equilibrium, the final result was identical within experimental error. Reversibility of the system is thus established and was confirmed by monitoring the charge-transfer band at 360 nm on cyclic acid–base treatment. On acid treatment (pH ~ 5) the oxygen complex is completely dissociated as noted by the disappearance of the characteristic uv peak, while subsequent titration to the original pH (10.5) quantitatively regenerates the oxygen complex. Extension over several acid–base cycles results in a slow decrease of the 360-nm band coupled with an increase in absorbance at ~ 560 nm, implying partial irreversible oxidation to a Co(III) complex.

Oxygen Uptake. Using the method described in the Experimental Section, equilibrium constants were determined from oxygen uptake, assuming that the change in dissolved free oxygen concentration was equal to the concentration of oxygen complex formed. The other concentrations could then be computed from the mass balance equations. The equilibrium constants thus obtained are in good agreement with those obtained potentiometrically, log $K_{O_2} = -4.2 \pm 0.1$ and -5.3 ± 0.2 for SEDDA and UEDDA, respectively.

Kinetics. The reaction of Co^{II}SEDDA and Co^{II}UEDDA with molecular oxygen is unusually slow. By running the experiments under pseudo-first-order conditions, constants for the forward reaction k_1 and reverse reaction k_{-2} could be determined assuming the mechanism reported by Wilkins[2a]

$$ML + O_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} MLO_2 \tag{6}$$

$$MLO_2 + ML \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} M_2L_2O_2 \tag{7}$$

Assuming a steady state in the intermediate, MLO2, one can easily derive the relationship

$$\frac{d[O_2 \text{ complex}]}{dt} = \frac{k_1 k_2 [ML]^2 [O_2]}{k_{-1} + k_2 [ML]}$$

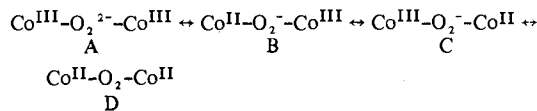for initial rates. A complete description has been given by Wilkins.[8]

Under the conditions investigated, utilizing a relatively high concentration of ML ([ML] > 0.01 M) gives $k_2[ML] \gg k_{-1}$ so that d[complex]/dt = k_1[ML], thus giving the observed first-order dependence on [ML]. k_{-2} can be obtained in separate experiments utilizing acid-catalyzed decomposition of the complex. The results are tabulated in Table IV.

Discussion

The ligand protonation constants, chelate formation constants, and chelate protonation constants as defined in eq 1–3 and tabulated in Table II are in good agreement with the previously reported values.[15] The depression of the chelate curve below the curve obtained for the free ligand in the high-pH region beyond $a = 2$ indicates the presence of chelate hydrolysis. These constants had not been previously reported but are reasonably close to those reported for the SDTMA–Co^{II} system ($K_{MLOH} = 10^{10.24}$ (DTMA), $10^{10.60}$ (SEDDA), $10^{10.75}$ (UEDDA)). The higher value for the EDDA systems is probably due to the fact that the hydrolyzed chelate must assume an overall negative charge for the

Co^{II}–EDDA system, while the Co–(DTMA)OH system is uncharged.

Under an oxygen atmosphere, the depression of the curve indicates formation of a stable species, probably best considered as a resonance hybrid of the formal canonical forms A–D.[16]

$$Co^{III}\text{-}O_2{}^{2-}\text{-}Co^{III} \leftrightarrow Co^{II}\text{-}O_2{}^{-}\text{-}Co^{III} \leftrightarrow Co^{III}\text{-}O_2{}^{-}\text{-}Co^{II} \leftrightarrow$$
$$\quad\quad\text{A}\quad\quad\quad\quad\quad\text{B}\quad\quad\quad\quad\quad\text{C}$$

$$Co^{II}\text{-}O_2\text{-}Co^{II}$$
$$\quad\quad\text{D}$$

In this case, the contribution from form A would be expected to be by far most important, since the increased affinity of the ligand for the cobalt ion indicated by the depression of the titration curve would be best explained by considering the complex to contain cobalt(III).

In the case of the Co–UEDDA–O2 complex, the inflection at $a = 2.5$ is discernible, indicating probable formation of a μ-hydroxo bridge. The lack of such an observed inflection in the Co–SEDDA–O2 system may be explained by the (strong) buffering properties of high-pH solutions. Supporting the assignment of a second bridge formation in both cases is the strong dependence of the equilibrium constant on pH. For a simple peroxo-bridged complex, such a marked dependence would not be expected.

The invocation of a dibridged complex also helps explain the unusually high-pH requisite for complex formation. The equilibrium constant for the oxygenation reaction is quite small (log K_{O_2} = -4.2 and -5.3 for SEDDA and UEDDA, respectively). For the reaction written

$$2ML + O_2 + H_2O \rightleftharpoons M_2L_2O_2OH + H^+$$
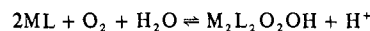
as the pH decreases, the equilibrium must shift to the left to compensate. Thus at low pH, the oxygen complex cannot form to any appreciable extent. Furthermore, in the low-pH region, any complex formed would only be a singly peroxo-bridged species which would be expected to be more labile and rapidly revert to the simple chelate. This dibridging (μ-peroxo-μ-hydroxo) has been found to occur in all cases in which there are two cis sites available for bridge formation. Thus the probable structures of the complexes are **1** and **2**.
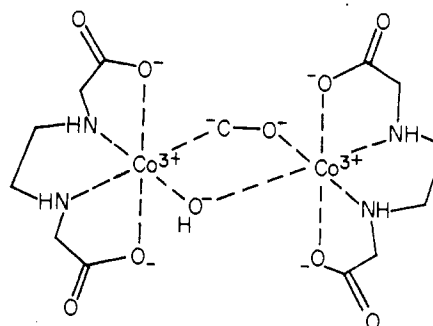
1, Co^{II}–SEDDA–O2 complex
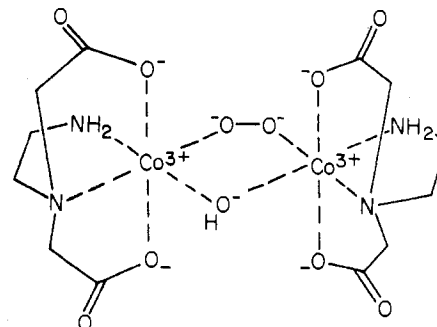
2, Co^{II}–UEDDA–O2 complex

For both the Co^{II}–SEDDA and Co^{II}–UEDDA complexes

Table V. Kinetic Parameters for CoL Oxygenation[a]

L	$k_1, M^{-1} sec^{-1}$	Ref
SEDDA	25	This work
UEDDA	22	This work
Triethylenetetramine	2.5×10^4	10
Tetraethylenepentamine	$\sim 10^5$	8
Histamine	1.8×10^4	8
Bis(ethylenediamine)	4.7×10^5	8
SDTMA	2.3×10^3	5
UDTMA	2×10^4	5
TREN	2.8×10^3	14

[a] At 25°, $\mu = 0.2 M$.

the oxygenation reaction is quite slow. As shown in Table V, values of k_1 for previously studied systems generally fall in the range 10^3–10^4, whereas for the EDDA–Co systems the rate constant is about 2 orders of magnitude lower. Since the EDDA systems are structural analogs to the polyamine (trien, tren) and amino acid (UDTMA, SDTMA) systems listed, there is little reason to expect that stereochemical differences in the complexes explain the rate differential observed.

It is unfortunate that the broad charge-transfer band effectively obscures the d–d bands within the complexes, so that spectral analysis of the complexes cannot readily be undertaken, and we thus have little quantitative information on the nature of the d-electron distribution which might clear up such difficulties.

Thus, the reasons for this anomalous kinetic behavior are not clear. As a requirement for oxygen binding, however, it seems apparent that the metal center must be able to donate (to some degree) an electron to the electrophilic molecular oxygen as presented in the foregoing resonance forms.

Such a transfer from the metal d orbitals to the π^* orbital of dioxygen is thought to be responsible for the high-intensity (M → L) charge-transfer band observed at 360 nm and is highly characteristic of the binuclear peroxo-bridged cobalt species. This electron transfer would be favored by ligands which can strongly donate electron density to the central metal making its (own) electrons more available for donation. Thus nitrogen coordination would tend to promote oxygenation, while oxygen coordination would be less favorable.

A cobalt(II) complex with a ligand such as EDDA with two nitrogen and two carboxylate donors would be expected on this basis to react less rapidly with dioxygen, since a larger energy of activation would be required for transfer of an electron in the transition state than in the case of a cobalt(II)–polyamine system (e.g., trien, tren) in which the ligand would be expected to donate electrons more strongly and facilitate the transfer.

In general, however, it can be noted that the trend noted by Fallab[6] that the inclusion of three nitrogens in the cobalt(II) coordination sphere comprises a minimal requirement for oxygen complexation is unsupportable, although it is obviously true that the ligand basicity may strongly influence the properties of the oxygen complex, thus the lowered reactivity and stability of the Co–EDDA complexes. Wilkins[2a] has previously noted the apparent complexation of oxygen by the Co[II]–SEDDA system, although no experimental details nor quantitative data were given.

Recently we have reported[5] the preparation and properties of cobalt oxygen carriers based on the isomeric diethylenetriaminemonoacetic acids (**3** and **4**) as ligands. These systems are unique in that they undergo no measurable decomposition

3, SDTMA   **4, UDTMA**
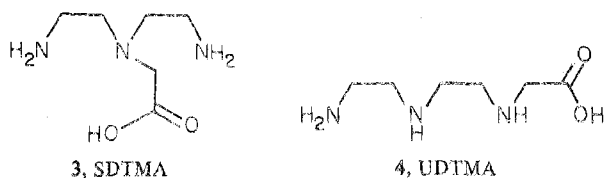
to cobalt(III) products and are readily reversible to nitrogen. Whatever electronic factors are responsible for these unusual and important properties have been modified in EDDA (the diacetic acid analog of DTMA) so that an irreversible oxidation to cobalt(III) products goes to completion within several days. The UEDDA–Co[II]–O₂ complex reacts more slowly to give the final cobalt(III) product, requiring several days, while the SEDDA-based system is completely oxidized within 18 hr. This difference may be attributable to steric differences between the ligands. The analogous Co–tren–O₂ system decomposes more slowly than the Co–trien–O₂ system, re-

tren   trien
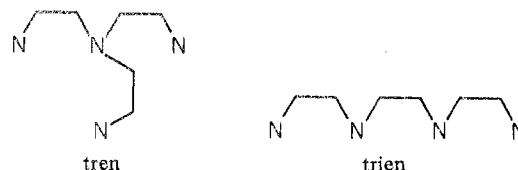
quiring several months for measurable oxidation to occur.[9] Thus it may be that the tripod-like ligand structure of tren and UEDDA inhibits final oxidation.

Studies on this question are proceeding in this laboratory. Qualitatively, however, it appears that the DTMA-based systems are unique in their complete lack of oxidation. Thus it appears that the balance of oxygen and nitrogen donation in the DTMA–Co[II]–O₂ complexes affords an environment which provides outstanding kinetic stability to these complexes not found in either the tetraamine or dicarboxylic acid analogs of DTMA. Such stability must almost certainly be kinetic, as the final oxidation products would be expected to be thermodynamically more stable than the intermediate oxygen adduct.

This work thus helps define the requisites for oxygen coordination by disproving the "3N" rule. Furthermore, as the binuclear cobalt oxygen carriers have shown promise as catalytic systems[17] and thus as models for enzymic systems, this study is valuable in delineating the nature of the electronic and steric factors which should be considered in ligand design for such catalysts, to control the important properties of reversibility and stability toward irreversible oxidation. Work along this line is continuing in these laboratories.

References and Notes

(1) (a) This work was supported by a research grant, A259, from the Robert A. Welch Foundation. (b) University Health Fellow.
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