

vironment of oxygens from the O^{2-} , OH^- , and H_2O ligands. The distribution of these ligands about any one iron atom would account for the large line widths observed in the Mössbauer spectra. It might be tempting to compare the Mössbauer parameters for the two sites to those observed in β -FeOOH where one site was considered to be Fe^{3+} in structural octahedra and the other is Fe^{3+} in channels in the crystal lattice.²⁰ However, this explanation for the spectra of β -FeOOH has been criticized by Childs et al.¹⁹ In any case the structure of the $Fe(OH)_3$ powder is quite different from that of β -FeOOH, and any speculation along these lines would be misleading.

Childs et al.¹⁹ also reject the idea that the surface iron gives rise to the second iron site in β -FeOOH and conclude that Cl^- , with extra protons to balance the charge, is responsible for the multiple sites in their samples. We have no such coordinating halide ions in our samples, and the presence of surface sites and bulk sites appears to satisfactorily account for our spectra. X-ray diffraction and magnetization measurements both lead to a particle diameter of 70–80 Å for $Fe(OH)_3$ powder. Using this diameter and assuming a spherical shape, we estimate the number of Fe^{3+} ions at the surface and, hence, in more distorted environments to be $\sim 15\%$ of a layer of 2 Å, the approximate Fe–O distance, is considered. However Voznyuk et al.²² have proposed that surface layers 10 Å thick should be considered, and this would raise the proportion of the surface iron to $\sim 50\%$. As the particle shape is likely to be irregular, a layer much thinner than 10 Å could give rise to the ratios of the two sites observed in our spectra.

Magnetization and susceptibility data characterize three distinct regions of magnetic behavior in $Fe(OH)_3$ powder. The ^{57}Fe Mössbauer spectrum shows the expected doublet in region I of Figure 3a, the paramagnetic region according to susceptibility measurements, but also indicates the presence of some residual magnetic order. As mentioned this is consistent with

the different characteristic times of observation between Mössbauer and static magnetic measurements. In region III, $T < 100$ K, we observe deviations from superparamagnetic behavior in the bulk magnetic data, and the $T = 77$ K Mössbauer measurements show that a substantial fraction of the sample is magnetically ordered. At 4.2 K the entire sample is ordered. At present we have insufficient data to better characterize the magnetically ordered region. The natural ferric gel $Fe(OH)_3 \cdot 0.9H_2O$ studied by Coey et al.¹¹ was shown to be sperimagnetic with antiferromagnetic nearest-neighbor exchange coupling, the Mössbauer measurements only showing magnetic ordering at 4.2 K. In regions I and II however the behavior is different for $Fe(OH)_3$ powder in that we observe an opposite deviation from the Curie–Weiss law, indicating the presence of a weak ferromagnetic component on the antiferromagnetic coupling. One might also expect the magnitude of the hyperfine field to decrease as the particle size decreases. This is found to be the case, and $Fe(OH)_3 \cdot 0.9H_2O$ has a field of 458 kOe and particle size of 40 Å, compared to the $Fe(OH)_3$ powder with one well-developed field of 486 kOe and another of 437 kOe with a much broader field distribution and a much larger particle size of 70–80 Å. We envisage this latter field as arising from these Fe^{3+} ions on, or close to, the surface of the particles. It is clear from the data presented here that $Fe(OH)_3$ powder has a structure different from either the $Fe(OH)_3$ gel or $Fe(OH)_3 \cdot 0.9H_2O$. We are currently attempting to obtain further structural information on these materials by EXAFS.

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Kinetics and Mechanism of the Reaction of (μ -Peroxo)bis[(bis(salicylaldehyde) ethylenediiminato)cobalt(III)] with Cyanide and Thiocyanate Ions

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It is shown that (μ -peroxo)bis[(bis(salicylaldehyde) ethylenediiminato)cobalt(III)] exists in aqueous solution as a dimer (four Co atoms, two oxygen molecules) with axial water ligands coordinated to the external Co ions regardless of the axial ligands present in the crystalline solute. The initial step in the reaction of this compound with cyanide or thiocyanate ions is dissociative exchange of the axial water. This is followed by rapid decomposition to Co(II) and molecular oxygen. This is contrasted with the behavior of ammine peroxo complexes of Co(III) that react by initial intramolecular electron transfer to give Co(II) followed by rapid ligand exchange. Either mechanism results in "anomalously" rapid ligand exchange in μ -peroxo Co(III) complexes.

Introduction

Many cobalt(II) compounds react with molecular oxygen to give isolable adducts. These compounds have been extensively studied. They are of interest both as intermediates in the oxidation of cobalt(II) and as models for biological oxygen-carrying systems. There have been several recent reviews of this area.^{1–4} Such complexes are of two general types,

namely those with a Co:O₂ ratio of 1 and those with a stoichiometry of two Co atoms to each O₂ molecule. The latter type are diamagnetic and correctly formulated as peroxo

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complexes of cobalt(III). This formulation is supported by X-ray crystallographic results⁵ and more recently by NMR studies.^{6,7} Several authors^{8,9} have noted that the ligand substitution reactions of these compounds are relatively rapid. At first sight this seems inconsistent with their formulation as Co(III) compounds, since the latter are notably inert to ligand substitution. The review of Jones, Summerville, and Basolo² remarks, "It is a curious fact that the peroxo ligand has a marked labilizing influence on the CoNH₃ bond" and that by McLendon and Martell¹ observes, "A more thorough investigation of the reactivity of these complexes towards substitution is warranted."

Recently Sasaki et al.¹⁰ have investigated the substitution of (μ -peroxo)bis[amminebis(ethylenediamine)cobalt(III)] ions by nitrite ions. They found that the rate of substitution was identical with that of decomposition to Co(II) and oxygen and also to the rate of conversion to the hydroxy-bridged oxygen complex. They concluded that all three reactions had a common rate-determining step, and it was suggested that this was electron transfer from the peroxide ion to the cobalt. Ligand exchange is completed by recombination of the substituted Co(II) with O₂. On this model the ligand exchange is rapid because it occurs at a Co(II) center. The lability of Co(II) compounds is well documented. Fallab et al.¹¹ reached a similar conclusion on the basis of isotopic oxygen-exchange studies.

The question then arises as to whether this explanation holds for all Co(III) peroxo complexes. Some such complexes have considerable stability at room temperature,⁴ and their rates of decomposition may be quite small. An example is provided by the complexes with the bis(salicylaldehyde) ethylenediamine ligand (abbreviated salen). These compounds have been extensively studied by Calvin and his collaborators¹²⁻¹⁴ and are of particular interest because of the reversible nature of the oxygen addition even in the solid state. The X-ray crystal structures of three compounds in this class have been reported.¹⁵⁻¹⁷ The Co(III) is octahedrally coordinated. Four coordination positions are occupied by the salen ligand and a fifth by the peroxo group. The sixth position is free to accept a solvent molecule, which can be replaced by other monodentate ligands, or to form a bridge with another salen molecule. The present paper reports a kinetic study of the replacement of solvent water in the parent salen complex by cyanide and by thiocyanate ions.

Experimental Section

The cobalt oxygen complexes were prepared by the method of Floriani and Calderazzo.¹⁸ They have the stoichiometry (Co(salen))₂O₂X₂ where X = dimethyl sulfoxide, dimethylformamide, pyridine, and water.

Kinetic measurements were carried out on a Durrum D110 stopped-flow spectrophotometer with deuterium and tungsten light sources. The optical path length was 2 cm and the syringe drive rate 30 mL/s with a gaseous nitrogen pressure of 70 psi. The dead time is 2-5 ms. Data were collected in digital form by using a Nicolet 1170 signal averager and checked from plots obtained with a Hewlett-Packard plotter. The estimated errors of the rate constants are $\pm 10\%$.

Solution molecular weights were measured by using an Hitachi Perkin-Elmer (Model 115) molecular weight apparatus. This utilizes the vapor pressure method and was calibrated with imidazole. Three separate determinations were carried out for each compound.

Proton NMR spectra were obtained on a Bruker WP80 FT spectrometer using deuterium (D₂O) locking. The operating temperature was 27 °C, and signals were referenced to internal Me₄Si. ⁵⁹Co spectra were obtained on a Bruker WH90 FT spectrometer operating at 21.252 MHz. The reference was aqueous potassium cobalticyanide (external). UV/visible spectra were measured on a Pye Unicam SP8-100 double-beam instrument.

Results

(a) Solution Structure of Co salen Complexes. The three X-ray structures of these complexes published¹⁵⁻¹⁷ gave rather different results. In one case¹⁵ the complex was dimeric, containing two oxygen molecules and four Co atoms, with solvent molecules occupying the sixth positions of the exterior Co atoms. The interior Co atoms were bridged by oxygen atoms from the salen ligands. In the other structures the molecule was monomeric with solvent coordinated to both Co atoms. In the "monomeric" structures the axial ligands were DMF and piperidine. In the "dimeric" structure the axial ligand was water. The solid compounds we have prepared contain pyridine, Me₂SO, DMF, and water as axial ligands. They are decomposed to Co(II) and O₂ by solvents other than water. They are stable in water with no significant change in optical absorption spectrum on standing overnight. The questions then arise as to whether these aqueous solutions contain "monomeric" or "dimeric" complexes and whether the axial ligand is water or another solvent. Molecular weights were therefore measured in water for the aquo complex and for the Me₂SO compound. For the aquo complex, the measured molecular weight was 1408 \pm 30 compared with calculated values of 1401 and 719 for the dimer and monomer, respectively. This compound is clearly dimeric in aqueous solution. For the Me₂SO complex, a value of 1321 \pm 50 was obtained. This may be compared with calculated values of 839 and 1521 for the monomer and dimer containing Me₂SO respectively. This again indicates a predominance of the dimer but does not determine the nature of the axial ligand.

This question was resolved by proton NMR experiments. Solutions of all the complexes prepared gave identical NMR spectra in D₂O except for the appearance of appropriate "solvent" lines (pyridine, Me₂SO, DMF). Further, the observed chemical shifts of the solvent resonances are within experimental error identical with those obtained from solutions of Me₂SO or DMF of the same concentrations. The shifts are not affected by dilution or by adding small amounts of Me₂SO or DMF. Rapid exchange between free and complexed Me₂SO or DMF is therefore unlikely. We conclude therefore that the replaceable ligand in the reactions described below is water irrespective of the choice of complex. Since the Me₂SO compound proved to be the easiest to isolate, it has been used in the kinetic experiments described below.

The dimeric structure indicated by the molecular weight measurements is consistent with the X-ray crystallographic findings for water as an axial ligand. An attempt was made to confirm this solution structure by ⁵⁹Co NMR. Two separate resonances should be observed for the "inside" and "outside" Co atoms. In aqueous solution a single broad line with chemical shift 8369 ppm (relative to cobalticyanide ion) and line width of 12 850 \pm 1500 Hz is observed. The chemical shift is consistent with those of other Co O₂ complexes.⁶ Since

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Table I. Pseudo-First-Order Rate Constants

X ⁻	[X ⁻], M	k _{obsd} , s ⁻¹
CN ⁻ ^{a,b}	0.10	0.0200 ± 0.0085
	0.25	0.0439 ± 0.0072
	0.50	0.0620 ± 0.0113
	0.75	0.0925 ± 0.0056
	1.00	0.1104 ± 0.0060
	1.50	0.1246 ± 0.0040
NSC ⁻ ^{a,c}	2.00	0.1385 ± 0.0040
	0.15	0.0127 ± 0.0080
	0.20	0.0170 ± 0.0064
	0.33	0.0303 ± 0.0091
	0.50	0.0353 ± 0.0064
	0.75	0.0572 ± 0.0100
	1.00	0.0611 ± 0.0050
	1.25	0.0810 ± 0.0064
	1.50	0.0833 ± 0.0050
	1.75	0.0840 ± 0.0064

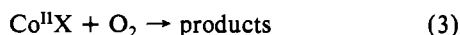
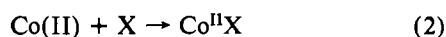
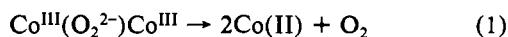
^a [(Co(salen))₂O₂(H₂O)]₂ = 0.11 mM, 460 nm ($\epsilon = 8.9 \times 10^2$ M⁻¹ cm⁻¹) shoulder; I = 4.5 M (NaClO₄); 24 °C; pH 7.0 (0.2 M Na₂HPO₄-0.2 M NaH₂PO₄). ^b Reaction followed at $\lambda_{\max} = 448$ nm ($\epsilon = 1 \times 10^3$ M⁻¹ cm⁻¹). ^c Reaction followed at $\lambda_{\max} = 470$ nm ($\epsilon = 725$ M⁻¹ cm⁻¹).

the line is so broad, the inability to resolve the resonances of the inside and outside Co atoms is perhaps not surprising.

(b) Kinetic Experiments. The reactions of the Co(salen) oxygen complex with cyanide and with thiocyanate ions have been studied. In both cases oxygen is evolved and the presence of Co(II) in the resulting solution is shown by its visible spectrum. The spectrum of the solution is consistent with the presence of Co^{II}salenX with X = cyanide or isothiocyanate. On prolonged standing the final product of the reaction is Co^{III}salenX₂⁻. The potassium salt of the thiocyanato compound was isolated in 70% yield after being allowed to stand in air for 3 weeks and characterized by X-ray crystallography.¹⁹ The reactions were examined at 24 °C and pH 7.1 in phosphate buffer at an ionic strength of 4.5 M (NaClO₄). The kinetics of the initial reactions were studied by means of stopped-flow spectrophotometry.

The solubility of the cobalt complex is limited, and a concentration of 0.11 mM (assuming the molecular weight of the dimer) was used throughout. Added ligand concentrations varied from 0.1 to 2.0 M at a total ionic strength of 4.5 M. The reactions were followed at 448 and 470 nm for CN and NCS substitution, respectively. Good exponential formation curves were observed at both wavelengths indicating a pseudo-first-order reaction. The k_{obsd} values obtained are given in Table I. Bubbles due to oxygen evolution produced only modest disruption of the stopped-flow traces, and it appears that formation of oxygen does not occur in the first step of the reaction. A second step can be observed for the thiocyanate reaction, but oxygen bubbles prevented the acquisition of quantitative data. It is likely that this reaction is faster with the cyanide ion since no second reaction can be clearly discerned and there is markedly more interference from bubbles in the first step.

These results differ from those reported by Sasaki et al.¹⁰ in that k_{obsd} clearly depends on the concentration of added ligand. Plots of k_{obsd} vs. [X⁻] are shown in Figure 1. A mechanism (eq 1-3) involving an initial intramolecular redox



step could only give the plots of Figure 1 if the rate of the

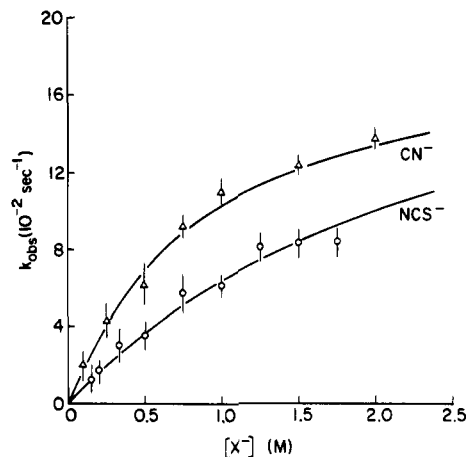
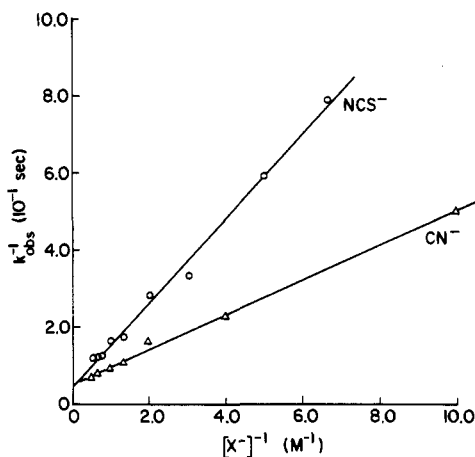
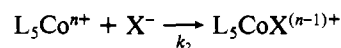
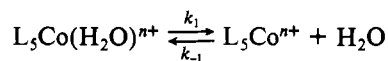
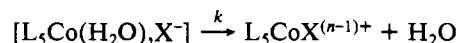
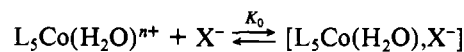
Figure 1. Variation of k_{obsd} with ligand concentration.

Figure 2. Double-reciprocal plots for ligand substitution reactions.

second step was comparable to that of the first step. This seems unlikely since the first-order rate constants for water exchange at Co(II) are typically of the order 10⁶ s⁻¹.²⁰ A more attractive possibility is that the observed reaction is ligand substitution of the initial oxygen complex. It is usual to distinguish four ligand substitution mechanisms: associative (A), dissociative (D), and interchange (I_a or I_d).²⁰ An associative mechanism would normally lead to a linear plot of k_{obsd} vs. [X]. The plots of Figure 1 are clearly not linear. The lack of linearity could be ascribed to medium effects since relatively high concentrations of ligand are involved but, as has been discussed by Haim and Wilmarth,²¹ this is unlikely for Co(III). A dissociative



or interchange



method is therefore indicated. Since the axial water ligands are well separated, we assume they react independently. In

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Table II. Slopes and Intercepts of $1/k_{\text{obsd}}$ vs. $1/[X^-]$ Plot

ligand	D		I_d or I_a		
	k_2/k_{-1}	k_1, s^{-1}	$kK_0, M^{-1} s^{-1}$	k, s^{-1}	K_0, M^{-1}
CN ⁻	1.163	0.192 ± 0.02	4.877	0.192	23.42
NCS ⁻	0.443	0.208 ± 0.02	10.857	0.208	52.27

Table III. $k_{\text{ex}}(\text{H}_2\text{O})$ for Co Complexes^a

complex	k_{ex}, s^{-1}	$T, ^\circ\text{C}$	pH
Co(H ₂ O) ₆ ²⁺	1.10×10^6	25	7.2
Co(HP)(H ₂ O) ₅ ³⁺ ^b	1.70×10	25	7.2
trans-Co(NH ₃) ₄ SO ₃ (H ₂ O) ⁺	1.34×10	25	
[(Co(salen)) ₂ O ₂ (H ₂ O)] ₂	2.00×10^{-1}	24	7.1
Co(CN) ₅ (H ₂ O) ²⁻	1.00×10^{-3}	40	
Co(NH ₃) ₅ (H ₂ O) ³⁺	6.00×10^{-6}	25	

^a Data from: Wilkins, R. G. "The Study of Kinetics and Mechanisms of Transition Metal Complexes"; Allyn and Bacon: New York, 1974. ^b HP = hematoporphyrin.

both cases it is predicted that a plot of $1/[X]$ vs. $1/k_{\text{obsd}}$ will be linear, i.e., either

$$\text{D: } \frac{1}{k_{\text{obsd}}} = \left(\frac{k_{-1}}{k_1 k_2} \right) \frac{1}{[X^-]} + \frac{1}{k_1} \quad (4)$$

or

$$\text{I: } \frac{1}{k_{\text{obsd}}} = \left(\frac{1}{kK_0} \right) \frac{1}{[X^-]} + \frac{1}{k} \quad (5)$$

Figure 2 shows the appropriate reciprocal plots. They are clearly linear with a common intercept for both of the substituting ligands. The interpretation of the slope and intercept depends on whether the mechanism is dissociative or interchange. The derived parameters for the two alternatives are given in Table II. For an I_a mechanism we would expect k to be different for NCS⁻ and CN⁻ since, by definition, bond forming influences the rate. Within experimental error the k 's are the same. The mechanism is therefore either D or I_d . If it is I_d , we obtain the equilibrium constant K_0 from the slope. K_0 may be estimated from the modified Fuoss relationship²² as presented by Rorabacher²³ for the case in which one of the reactants is uncharged. For the usual metal complex radii of 3 or 4 Å these calculations give K_0 around 0.1–0.2 M⁻¹ in agreement with experimental determinations.²² For a radius of 10 Å, the maximum expected for the present complexes, a K_0 of 2.52 M⁻¹, is calculated. This is considerably less than the values of 20–50 M⁻¹ contained in Table II. We conclude therefore that the data are not consistent with an I_d mechanism and that a D mechanism is indicated.

Confirmation of this conclusion is obtained by comparing the ratios of k_2/k_{-1} shown for the D mechanism in Table II with literature values obtained for other Co(III) complexes.^{20,23–25} The observation that CN⁻ is a rather better nucleophile than NCS⁻, which is the implication of the ratios in

Table II, parallels that of Halpern et al.²⁴ for (sulfito)pentaamminecobalt(III), which also undergoes substitution by a D mechanism.

Since we have established by NMR that the species in solution is an aquated dimer and by kinetic measurements that the initial reaction is a dissociative ligand exchange, it follows that the common rate constant k_1 (0.2 s⁻¹) measures the rate of breaking the Co–water bond. It remains to be discussed whether this is a reasonable value for such a process. Table III contains literature data for water-exchange reactions for a number of cobalt complexes. Although the rate for the "typical" complex, Co(NH₃)₅H₂O³⁺, is much lower than that found in the present study, there are a number of examples showing rates equal to or greater than that we report. These are associated either with compounds containing extended π systems such as porphyrins or with trans-activating ligand such as sulfite. Extended π systems appear to stabilize the five-coordinated intermediate required for a dissociative exchange. There have of course been extensive discussions of the reasons for such stabilization in the isoelectronic Fe(II) porphyrins. We conclude therefore that the observed rate is reasonable for a complex containing the planar salen π system.

Finally we inquire why the mechanism for ligand exchange found in the present study differs from that reported by Sasaki et al.¹⁰ This mechanism seems well established and is supported by the earlier results of Fallab and collaborators^{26,27} on similar ammine complexes. The implication is that for ammine dioxygen complexes intramolecular electron transfer is faster than axial ligand dissociation, but for salen dioxygen complexes the converse is true. We note that the first-order rate constant found by Sasaki ($5 \times 10^{-3} s^{-1}$) is almost 2 orders of magnitude less than the dissociation rate we report. With a planar π ligand stabilizing the five-coordinated intermediate axial ligand, dissociation is rate determining. Without one, electron transfer is rate determining. Either case leads to "anomalously rapid" ligand exchange.

The final products of the reactions are also different. In the case of the amines the substituted dioxygen complexes are stable. In the case of the salen complexes they are not. The cyanide or thiocyanate oxygen complexes readily lose oxygen to give Co(II) compounds and more slowly autooxidize to Co(III) complexes. Intramolecular electron transfer from the peroxide is clearly fastest with a cyanide trans to the peroxide, rather slower with thiocyanate, and much slower with water. This is probably not unreasonable in light of the discussions of the electronic structures of Co O₂ complexes by Gall et al.,²⁸ Carter et al.,²⁹ Floriani and Calderazzo,¹⁸ and others. A π -accepting ligand such as cyanide competes with the oxygen for electron donation from the Co, leaving the oxygen environment more similar to that of dioxygen and less like that of peroxide. This would be consistent with more rapid dissociation to dioxygen.

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