

similarity in biological activity observed for thiosugar analogues of auranofin in an animal model for rheumatoid arthritis.⁸

Biological studies in animal models for rheumatoid arthritis have demonstrated that oral absorption is characteristic of gold(I) compounds in which at least one ligand is a phosphine.²⁰ Oral absorption is demonstrated by atomic absorption measurements, which quantitate the concentration of gold in the serum following oral administration. This observation is consistent with the lipophilicity of the phosphine ligand, since lipophilicity facilitates membrane diffusion. The results of our study are consistent, as a model study representing the much more complicated biological system, with this biologically derived correlation between oral absorption and chemical structure.

Relatively few kinetics studies of gold(I) compounds have been previously reported,^{4,22} and there are none in which the medicinally important phosphine ligand is present. It should be noted that

the phosphine ligand stabilizes the +1 oxidation state of gold in aqueous solution.⁴ The oxidation-reduction chemistry of this class of compounds remains largely unexplored⁸ but may be an important factor in the biological effects of these compounds.²³⁻²⁵

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Oxidation of Cobalt(II) Amine Complexes to Mononuclear Cobalt(III) Complexes by Dioxygen

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The mechanism of the reaction of (ethylenediamine)(diethylenetriamine)cobalt(II) complexes with dioxygen to give the mononuclear cobalt(III) compound has been investigated by using ⁵⁹Co NMR. The use of this method enables the concentrations of the initially formed peroxo compounds and of the mononuclear cobalt(III) complexes to be monitored concurrently. It is concluded that the peroxo compounds are intermediates in the formation of the mononuclear cobalt(III) complex. The suggested mechanism involves reduction of the peroxo complex by cobalt(II). This reaction proceeds significantly faster for one isomer of the peroxo complex than for the other.

Introduction

The preparation of cobalt(III) amine complexes by oxidation of the corresponding Co(II) compounds with air has been well-known for many years. It is a standard experiment in most undergraduate inorganic laboratory courses. In spite of this familiarity there are still uncertainties regarding the mechanisms by which the Co(III) compounds are formed. Fallab and Mitchell¹ have discussed the problems in this area in a recent review.

The initial products of the reaction have been well characterized as (μ -peroxo)dycobaltate(III) complexes. These compounds are of limited stability and eventually decompose, in a manner that is usually described as "irreversible", to give mononuclear Co(III) complexes. The half-life for this decomposition varies from less than a second to several days depending on the nature of the ligands. The mechanism of this step is uncertain. It is of course not necessarily true that it will be the same for all ligands.

The simplest mechanism would be to form the peroxo complex from Co(II) and dioxygen and then to hydrolyze this complex to give the Co(III) complex and hydrogen peroxide. This implies that hydrogen peroxide should be formed in stoichiometric quantities. In two cases this has been observed. The first involves the cyano complex² and the second the trans dinitrobis(ethylenediamine) complex.³ In these two cases the decomposition occurs under acid conditions (pH ~ 1). Most other cobalt peroxo complexes decompose to Co(II) and dioxygen under these conditions and only give the Co(III) complex in neutral or alkaline solution. Shibahara et al.³ have discussed the role of strong-field ligands in favoring hydrolysis to Co(III) and hydrogen peroxide.

Although there have been claims to the contrary, it now seems to be accepted that hydrogen peroxide is not present during the irreversible decomposition of cobalt peroxo complexes to the Co(III) compounds except for the above complexes under strongly acid conditions.¹ An alternative mechanism is therefore required.

There are several possibilities. Hydrogen peroxide may indeed be formed but catalytically decomposes immediately to dioxygen and water. A number of salts and complexes of cobalt are known to catalyze this reaction.⁴ This would require the release of a stoichiometric quantity of oxygen, and although, in some cases, oxygen has been reported as a product, the evidence indicates that it is not formed in stoichiometric quantities.¹ In such instances it becomes questionable whether the peroxo compounds act as intermediates in the formation of the Co(III) complexes. Thus Stadtherr et al.⁵ suggest: "The simplest interpretation of those systems in which no hydrogen peroxide can be detected nor oxygen reemitted upon formation of mononuclear Co(III) complexes is that these complexes are not formed from the binuclear peroxo-cobalt(III) complexes. The peroxo complexes in these cases are unreactive species formed in a side reaction." It has been suggested that reduction of the peroxide moiety to water is accompanied by oxidation of the ligands.^{6,7} This mechanism seems to be

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particularly associated with peptide and dipeptide ligands. Fallab and Mitchell¹ also raise the possibility that the peroxo complexes may be further reduced by unreacted Co(II) complexes but remark that this hypothesis is unproved.

The present paper is concerned with the application of ⁵⁹Co NMR to the elucidation of these mechanisms. This spectroscopic technique can easily distinguish not only between the peroxo and the mononuclear Co(III) complexes but also between different isomers of both types of compounds.⁸ In a suitable system the concentrations of both the peroxo complexes and the mononuclear compounds can be concurrently monitored. This feature offers an approach to investigating whether the peroxo complexes are intermediates or side products in the formation of cobalt(III) amine complexes. It is necessary to choose a ligand system for which the peroxo complexes are sufficiently stable for easy observation and for which formation of the mononuclear complexes is also relatively facile. The absence of alternative reaction products such as bridged complexes is also desirable. The oxidation of Co²⁺ in the presence of stoichiometric quantities of en and dien to [Co^{III}(en)(dien)Cl]²⁺ (en = ethylenediamine; dien = diethylenetriamine) is suitable.

Experimental Section

⁵⁹Co NMR spectra were obtained on a Bruker WM250 spectrometer operating at 59.04 MHz. In the present experiments it is necessary that the NMR spectra be obtained in as short a time as possible so as to minimize changes in solution composition during spectral acquisition. On this NMR instrument acceptable spectra can be obtained in 5 min or less by using 800–1000 90° pulses with no delay between pulses. Solution concentrations of around 0.1 M or more in each compound are desirable. The starting solutions were therefore prepared by mixing 0.5 M aqueous solutions of CoCl₂·6H₂O, en, and dien. The pH of this mixture is approximately 6. The reaction proceeds at a suitable rate at 45 °C. The NMR probe temperature is 24 °C at which temperature the reaction proceeds relatively slowly. The reaction mixture was therefore heated to 45 °C and a steady stream of air passed through. Samples were withdrawn from the reaction mixture at measured time intervals, placed in NMR tubes, flushed with argon to remove any remaining air and immediately frozen in dry ice to stop the reaction. Initially the samples were removed at 5- and 10-min intervals, increasing to 30 and 60 min as the reaction progressed. Monitoring ceased after 5 h. The chemical shift assignments of both the peroxo and mononuclear Co(III) complexes are known from previous studies⁸ in which both complexes were prepared by literature methods.^{9,10} Peak areas were obtained by counting squares. Proton spectra of both the starting materials and the final solutions were obtained to check for impurities and for possible ligand oxidation products. No resonances attributable to these sources were observed. Although we cannot exclude the possibility that there are side products in this oxidation reaction the only final product that we have been able to detect is the mononuclear ethylenediamine/diethylenetriamine complex and it seems clear that this is the principal product.

Two additional NMR experiments have been carried out. It has previously been demonstrated that the Co(III) peroxo complex can react with Fe²⁺ ions to give the mononuclear Co(III) complex.¹² It is pertinent to ask whether there is a similar reaction with Co²⁺ ions and with the complex formed between Co²⁺ and en and dien in stoichiometric amounts. These reactions can also be followed by monitoring the ⁵⁹Co NMR spectrum of the peroxo complex. The experimental conditions were chosen to facilitate comparison with the previous Fe²⁺ experiments. The peroxo complex was prepared by following the procedure of Duffy, House, and Weil.¹⁰ Its optical and NMR spectra agreed with those reported in the literature. In the first experiment 25 mM cobalt sulfate was reacted with 12.5 mM peroxo complex in a buffered solution at pH 4.5 and 24 °C. Conditions were similar in the second experiment except that the concentration of the peroxo complex was 20 mM and this solution was reacted with a solution 40 mM in each of Co²⁺, ethylenediamine, and diethylenetriamine. In both cases the intensities of the ⁵⁹Co resonances were measured as a function of time over a period of 5 h.

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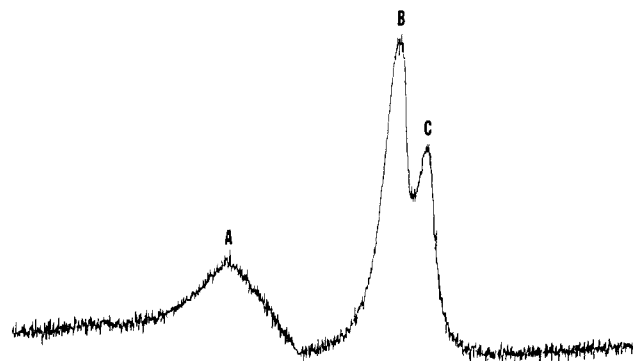


Figure 1. ⁵⁹Co NMR spectrum obtained immediately after commencing oxygenation: peak A (7700 ppm), [Co(en)(dien)Cl]²⁺ overlapping isomers; peak B (7604 ppm), *ad,bef,c* isomer of [(Co(en)(dien))₂O₂]⁴⁺; peak C (7585 ppm), *df,abe,c* isomer of the peroxo complex. (See ref 8 for assignments and nomenclature.)

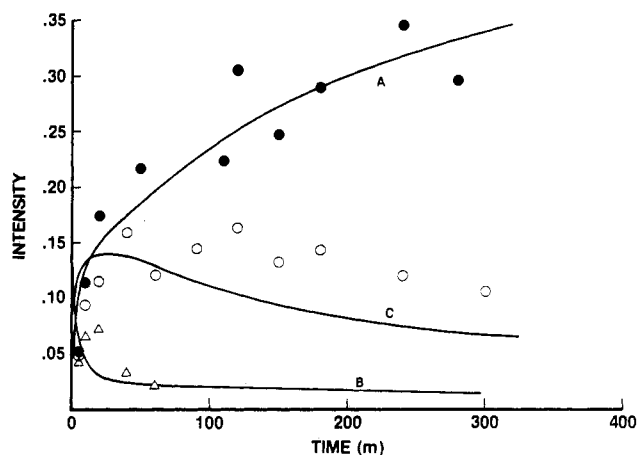


Figure 2. Variation of the intensities of peaks A (closed circles), B (triangles), and C (open circles) with time of oxygenation. The solid lines are calculated based on the mechanism described and the following rate constants: rate of formation of isomer B, 1600 M⁻¹ s⁻¹, and rate of decomposition of isomer B, 7.41 × 10⁻³ s⁻¹; rate of formation of isomer C, 800 M⁻¹ s⁻¹, and rate of decomposition of isomer C, 7.4 × 10⁻⁴ s⁻¹; rate of reaction of isomer B with Co(II), 0.1 M⁻¹ s⁻¹, and rate of reaction of isomer C with Co(II), 0.001 M⁻¹ s⁻¹.

The mechanistic interpretation of the NMR data requires some knowledge of the rate of formation of the peroxo complexes. Miller et al.¹¹ have reported such rates for the en and dien Co complexes but not for the complex containing both these ligands. Although the rate that can be estimated for the mixed complex by interpolation between the results for the simple amine complexes would probably suffice for qualitative calculations, it was decided to measure this rate in case it was considerably different. The procedure reported by Miller et al.¹¹ was followed quite closely. The experiments were performed at pH 9 in Tris buffer, at ionic strength 0.2 M (with KNO₃) and temperature of 24 °C. The CoCl₂ solutions were flushed with argon to remove oxygen. Ethylenediamine and diethylenetriamine solutions were similarly treated before mixing with the cobalt chloride. The reactions of mixtures containing 3 mol of en to 1 mol of CoCl₂, 2 mol of dien to 1 mol of CoCl₂, and 1 mol of en plus 1 mol of dien to 1 mol of CoCl₂ with buffer saturated with oxygen were examined. In the latter case the product is [Co(en)(dien)]₂O₂⁴⁺. The measured concentration of the oxygen solution was 2.3 × 10⁻⁵ M. The reactions were examined on a Durrum D110 stopped-flow spectrophotometer. Data were collected on a Nicolet 1170 signal averager. Pseudo-first-order conditions were maintained by using Co(II) solutions in the range 10⁻³–10⁻⁴ M. Absorbances at several wavelengths in the range 380–450 nm were monitored.

Results

Figure 1 shows a typical NMR spectrum. Better signal to noise can of course be obtained by accumulating more scans but at a cost of uncertainty in the reaction time. Peaks B and C at 7604 and 7585 ppm are assigned to isomers of the peroxo complex as reported previously.⁸ There is a third low concentration isomer with a resonance between the two shown, which is not resolved

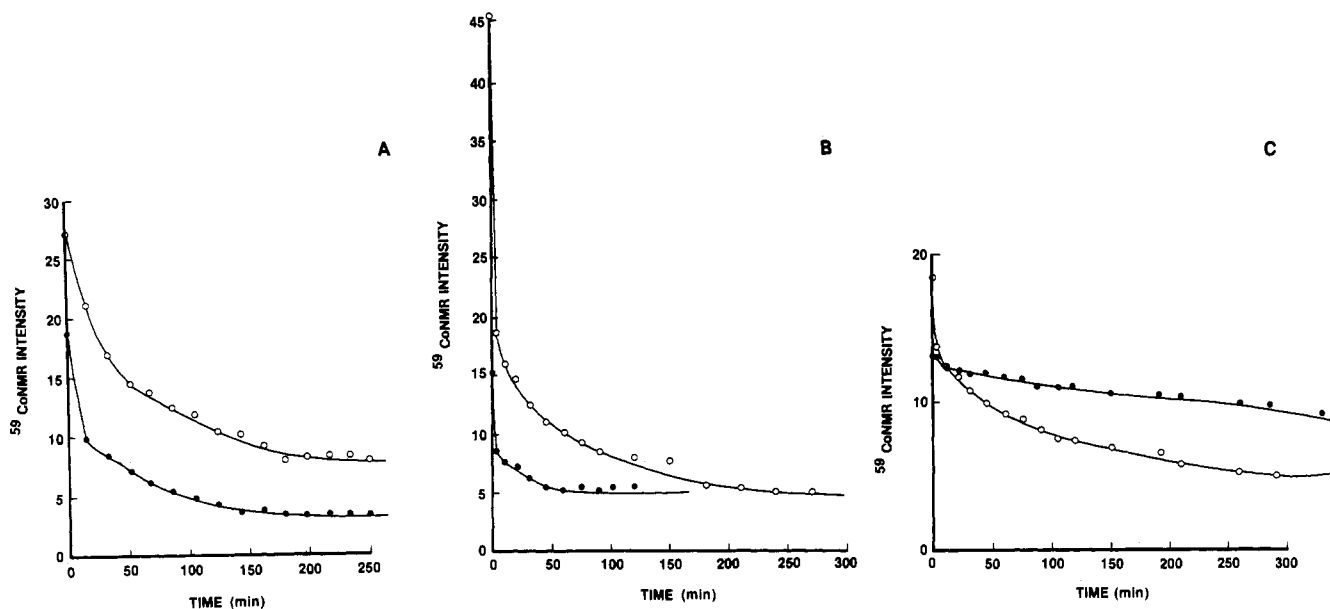


Figure 3. Variation of the intensities of the ^{59}Co NMR peroxo complex resonances during reaction with (A) Fe^{2+} ions (data from ref 12), (B) Co^{2+} ions, and (C) Co^{2+} with equimolar en and dien: open circles, isomer B; closed circles, isomer C.

under the present experimental conditions. The different isomers of $(\text{Co}(\text{en})(\text{dien})\text{Cl})^{2+}$ are unresolved in resonance A at 7700 ppm. The relative intensities of these three NMR lines are plotted as a function of reaction time in Figure 2. The maximum concentration of isomer B occurs too soon after the reaction commences to appear in the diagram. After about an hour it was no longer possible to measure separately the intensity of the weaker peroxo line. Beyond this point only a single peroxo resonance was measured, and this represents the intensity of all three isomers. The solid lines are derived from calculations based on the mechanism discussed below. After 1 h the experimental points should be compared with the sum of B and C.

There is clearly a fair amount of scatter in the NMR intensity data of Figure 2, but the following qualitative conclusions are unambiguous:

- There is a period in which the mononuclear complex is formed rapidly followed by a period of much slower growth.
- Both isomers of the peroxo complex reach a maximum concentration and then diminish.
- Isomer B is formed more rapidly and disappears more rapidly than isomer C.

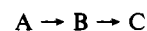
The results of the stopped-flow experiments can be summarized quite briefly. Under the conditions outlined in the Experimental Section good pseudo-first-order plots were obtained in all experiments. Following Miller et al.¹¹ the data were analyzed by plotting $[\text{Co}^{2+}]/k_{\text{obsd}}$ vs $[\text{Co}^{2+}]^{-1}$. The intercept of this plot gives the rate of formation, and the slope, when combined with an overall equilibrium constant, can be used to obtain the rate of the rate-determining dissociation step. With en as a ligand the measured second-order rate constant for the formation of the complex was $7.2 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$. This is in agreement with the literature value¹¹ of $\leq 10^4 \text{ M}^{-1} \text{ s}^{-1}$. With dien as a ligand we obtained $0.32 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$. This value is somewhat less than the literature value of $1.2 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$, which probably reflects small differences in the temperature, pH, and ionic strength conditions used. For the formation of the mixed-ligand peroxo complex a rate of $1.15 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ was obtained. The important point is that the rate of formation of $(\text{Co}(\text{en}(\text{dien}))_2\text{O}_2)^{4+}$ is similar to that of other complexes that have been examined and is quite rapid compared to the rate of formation of the mononuclear cobalt compounds. The rates quoted above refer to a temperature of 24 °C. Since the NMR data refer to a reaction temperature of 45 °C we can safely assume that the rate constant for the formation of the peroxo complex is $>10^3 \text{ M}^{-1} \text{ s}^{-1}$.

The results of the experiments in which the peroxo complex was reacted with $\text{Co}(\text{II})$ are shown in Figure 3. Figure 3A

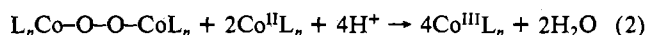
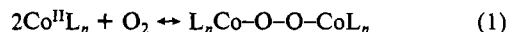
reproduces the previous result¹² for the reaction with Fe^{2+} ions. Figure 3B shows the analogous reaction with Co^{2+} ions. In both cases there is an initial sharp decrease in the intensity of the peroxo resonances followed by a slower decay. The initial rate seems to be somewhat higher with Co^{2+} than with Fe^{2+} . Figure 3C shows the reaction with Co^{2+} in the presence of the amine ligands. The decrease in intensity is much slower, indicating that ligand dissociation of the Co^{2+} is a necessary prerequisite for reaction. The difference in the rates of reaction of the two isomers is much more pronounced. The isomer corresponding to resonance C of Figure 1 reacts only very slowly. This behavior closely parallels the data for air oxidation shown in Figure 2.

Discussion

The above results are incompatible with a number of the mechanisms that have been suggested for the formation of the mononuclear $\text{Co}(\text{III})$ complexes. There is no evidence from the proton spectra obtained in the present work or from any report in the literature that ligand oxidation occurs with simple amine ligands. It is difficult to account for the rapid initial formation of large amounts of mononuclear complex by a simple reaction scheme of



in which B is the peroxo complex that decomposes directly to C, the $\text{Co}(\text{III})$ complex. This is true either for the case in which hydrogen peroxide is the other product or for the case in which the hydrogen peroxide is catalytically decomposed to dioxygen and water. We suggest that the mechanism which is most consistent with the data is one in which the peroxo complex reacts with $\text{Co}(\text{II})$ to further reduce peroxide to water, i.e.



Taken together these reactions lead to the four-electron reduction of O_2 to $2\text{H}_2\text{O}$ and the concurrent oxidation of four molecules of $\text{Co}(\text{II})$ complex to the $\text{Co}(\text{III})$ compound. Both the reactions proceed in two steps. For the first reaction, rates of the rate-determining forward and backward steps (averaged over the different isomers) were obtained from the stopped-flow data and an assumed equilibrium constant, by following the analysis of Miller et al.¹¹

At short reaction times substantial concentrations of both $\text{Co}(\text{II})$ and the peroxo complex are present, and the $\text{Co}(\text{III})$ compound is formed rapidly. After the reaction has proceeded from some time the only $\text{Co}(\text{II})$ present will be the very small concentration

that results from equilibrium 1, and further formation of mononuclear Co(III) complex will therefore be slow as is observed. Direct evidence for reaction 2 is provided by the results shown in Figure 3. These results also show that the difference in rates for the different isomers occurs predominantly in the second step. Thus in this mechanism the peroxo complexes are intermediates in the formation of the mononuclear Co(III) complex, but they are also side products to the extent that in the later stages of the reaction they must dissociate to give Co^{2+} ions before the reaction is completed.

Calculations have been carried out to simulate the curves of Figure 2, assuming the mechanism described above. To perform these calculations estimates are required for the forward and backward rate constants of the rate-determining steps in reaction 1 and for the rates of reaction of the different isomers with $\text{Co}(\text{II})$. The forward rate constant has been determined directly and the backward rate constant can be estimated from the slope of the plot in the stopped-flow experiments described (1.35×10^{-7}) together with estimates of equilibrium constants (10^9 for isomer B and 10^{10} for isomer C compared to the literature value of 3×10^8 for the dien compound¹¹). The rates of reaction 2 can be used as adjustable parameters. The values required to obtain reasonable

fits are smaller than those observed in the analogous Fe^{2+} reaction by factors of 10–1000. This parallels the much slower reaction of Figure 3C rather than that of Figure 3A. The solid lines of Figure 2 result from such a calculation, employing the constants given in the caption. At times greater than 1 h the comparison should be made between the experimental data and the sum of B and C. Clearly the quality of the NMR intensity data and the overlapping of the lines do not allow for any accurate estimation of the rate parameters, but the fact that the curves can be qualitatively reproduced by using rate constants that are reasonable by the above criteria provides support for the suggested mechanism.

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Registry No. $[\text{Co}(\text{en})(\text{dien})\text{Cl}]^{2+}$, 33847-42-6; *ad,bet,c*- $[(\text{Co}(\text{en})(\text{dien}))_2\text{O}_2]^{4+}$, 85281-60-3; *df,abe,c*- $[(\text{Co}(\text{en})(\text{dien}))_2\text{O}_2]^{4+}$, 85281-59-0; O_2 , 7782-44-7.

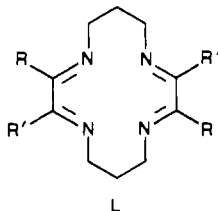
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Lewis Acidity of Cobalt(I)

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The synthesis, characterization, and reactivity of Co^{II} complexes of the macrocycles



are reported, where $L = L^1$ when $R = R' = \text{CH}_3$, $L = L^2$ when $R = \text{CH}_3$ and $R' = \text{Ph}$, and $L = L^5$ when $R = R' = \text{Ph}$. The complexes, denoted $\text{Co}^{\text{II}}L^{2+}$, undergo unusually facile one-electron reduction by a variety of reducing agents (e.g., Na/Hg, pyridine, *N*-methylimidazole) to the corresponding Co^{I} complexes in acetonitrile solvent. The $\text{Co}^{\text{I}}L^+$ complexes serve as potent Lewis acids toward a variety of monodentate ligands. The equilibrium constants, K_{eq} , for adduct formation between $\text{Co}^{\text{I}}L^+$ and the donors pyridine, 2,6-lutidine, *N*-methylimidazole, and Br^- have been measured by spectrophotometric methods and are reported herein. In general, K_{eq} increases with the donor ability of the monodentate ligand and with the electron-withdrawing ability of the macrocyclic ligand. A Lewis acid role for Co^{I} , which normally functions as a potent nucleophile, is highly unusual.

Introduction

Complexes of Co^{II} or Co^{III} containing macrocyclic ligands undergo metal reduction by potent reducing agents such as sodium amalgam and tetrahydridoborate(1–) to the corresponding Co^{I} complexes.^{1–7} The same processes can be carried out by controlled-potential electrolysis at appropriate potentials.^{8–10} Recently, a report of reduction of (tetraphenylporphyrinato)cobalt(II) ($\text{Co}^{\text{II}}\text{TPP}$) to $\text{Co}^{\text{I}}\text{TPP}^-$ by 2-methyl-2-propanethiolate has appeared,¹¹ and this is the first example of reduction of Co^{II} to Co^{I} using a sulfide reductant.

The Co^{I} species typically function as Lewis bases, reacting with a variety of organic electrophiles to produce Co^{III} complexes containing the cobalt–carbon σ bond.^{2–4,7,8} The possibility that Co^{I} might function as a Lewis acid under appropriate conditions has been mentioned only a few times in the literature. Weak

coordination of a fifth ligand to Co^{I} occurs in vitamin B_{12} ,¹² and a recent report indicates that Co^{I} is a better acid toward bipyridine

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