Oxygen Complexation by Cobaltous Chelates of Multidentate Pyridyl-Type Ligands. Equilibria, Reactions, and Electron Structure of the Complexes[1a]

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Abstract: The oxygenation and oxidation reactions of the cobaltous chelates $Co(bpy)_2$ and $Co(phen)_2$ are described. In both cases dibridged μ-peroxo-μ-hydroxo complexes are formed. For $Co(bpy)_2$, it has been possible to separate the oxygenation and olation reactions, so that the effect of dibridging on oxygenation may be evaluated. The conversion of the oxygenated species to the oxidized form has been studied, and evidence for geometrical isomerization is given. Finally, the electronic structure of a series of dioxygen adducts of cobalt complexes of pyridyl-type multidentate ligands is described through the analysis of both d-d spectra and pyridyl π-π^* bands.

The study of dioxygen complexation by transition metals (particularly Co(II)) has received considerable attention recently, both for its intrinsic interest, and as a model for biological phenomena.[2,3] In-depth quantitative studies of some carefully chosen systems have begun to result in a much closer understanding of the factors affecting oxygenation.[3-5] In particular it may be stated that the oxygenation reaction is best viewed as a reversible internal redox reaction, in which the metal is formally oxidized, and the dioxygen formally reduced. Evidence for this view has accumulated from a number of sources,[2-5] including ESR, uv-visible spectroscopy, and potentiometric equilibrium studies. Thus, binuclear cobalt μ-dioxygen adducts are best visualized as μ-peroxo-biscobalt(III) complexes. The oxygenation reaction is thus aided by good σ donors, and hindered by electron withdrawing ligands.[3b]

It has further been shown that a second, μ-hydroxo, bridge will form whenever a site can readily be made available on cobalt cis to the dioxygen bridge.[3a,5] The effect of the second bridge seems to be to "lock in" the peroxo oxygen, although a quantitative measure of this effect has heretofore been difficult, as the oxygenation and olation reactions were not easily separated.

While much is known about cobalt dioxygen adduct formation, a number of pertinent questions remain to be probed. (1) What is the nature of the electronic distribution in cobalt dioxygen complexes? (2) How do the ligands interact with metal and dioxygen in the ternary complex to modify the reactivity of cobalt toward oxygenation? (3) In cases where dibridging can occur what is the contribution of the second bridge to overall complex stability? (4) What pathways are followed by dioxygen complexes in decomposition to inert Co(III) products?

The systems chosen herein to attempt to answer some of these questions are the cobaltous chelates $Co(bpy)_2$, $Co(phen)_2$, Co(trpy)(bpy), and Co(trpy)(phen), where bpy = bipyridyl, trpy = terpyridyl, and phen = 1,10-*o*-phenanthroline. The latter two mixed ligand complexes have previously been reported in some detail by Huchital and Martell,[4] who demonstrated the unusual reactivity of these complexes toward dioxygen, both in their kinetic behavior, and in their facile combination with dioxygen at low pH. The simpler $Co(bpy)_2$ and $Co(phen)_2$ systems have been less well examined. A preparation for (μ-NH_2-μ-$O_2Co_2(bpy)_4$) and μ-NH_2-μ-$O_2Co_2(phen)_4$) has been published[6] and the redox chemistry of these amido bridged complexes examined.[7] $Co(phen)_2$ has been noted to absorb oxygen at neutral pH[8] but no quantitative equilibrium or spectral data are available for this complex.

Thus, with the aforementioned questions in mind, systematic study of these systems was undertaken for comparison with previously studied oxygen complexes.

Materials and Methods

Standard solutions of cobalt(II) were prepared from reagent grade $Co(NO_3)_2$ and standardized by EDTA titration with murexide indicator. Terpyridine and *o*-phenanthroline hydrochloride were obtained from J. Fredrick Smith Chemical Co. Bipyridine was obtained from Aldrich Chemical Co. Purity of the ligands was established by potentiometric titration. All potentiometric equilibrium determinations were performed in a jacketed cell at 25.0 °C using methods described previously.[3a,5] Ionic strength was maintained at 0.10 M with KNO_3, and the pH meter (Beckman Research Model) was standardized to read $[H^+]$ concentration directly rather than activity.

Oxygen atmospheres were prescrubbed with Ascarite to remove CO_2, and nitrogen atmospheres were serially scrubbed with Ascarite, acidic tin(II) chloride, and alkaline potassium pyrogallate to remove both CO_2 and O_2.

The spectra were measured with a Cary 14 recording spectrophotometer. Quartz cells with fixed path lengths ranging from 50 to 0.1 mm were employed as required. Water was used in the reference cell except when difference spectra were measured, in which case the reference cell contained *o*-phenanthroline hydrochloride adjusted to the same pH and concentration as that in the sample cell. Uv spectra were reproducibly obtained to ±1.0 nm.

Oxygen uptake measurements were performed at 25.0 °C (0.10 M KNO_3) using a polarographic oxygen sensor (Yellow Springs Instrument Co.).

Results and Discussion

Potentiometric equilibrium studies (Figure 1) of $Co(bpy)_2$ and $Co(phen)_2$ reveal an initially rather surprising fact. Unlike the superficially similar [Co(trpy)(bpy)] which forms a strong dioxygen adduct at pH 2, the $Co(bpy)_2$ and $Co(phen)_2$ systems are relatively unaffected by dioxygen until the neutralization equivalent exceeds $a = 2$ (a = millimoles of base/millimoles of metal), upon which the chelate solutions turn brown (λ_{max} 390 nm) under oxygen, indicating the presence of a dioxygen adduct.[2-4] In these systems, an additional 0.5 mol of hydroxide is consumed per mole of cobalt, indicating formation of a μ-hydroxo bridge,[5] which apparently serves to "lock in" the peroxo bridge, thereby shifting the equilibrium toward the oxygenated species. Thus by measuring oxygen uptake in the lower (a = 0-2) and upper (a = 2-2.5) buffer regions, an independent measure can be obtained of oxygen complexation in the presence and absence of a hydroxo bridge. We may define the constants $K_{O_2} = [ML_2O_2ML_2]/[ML_2]^2[O_2]$ for the low pH buffer region, and $K_{O_2,OH} = [H^+][ML_2O_2OHML_2]/[ML_2]^2[O_2]$ for the high pH region. Combining these constants gives:

$$\frac{K_{O_2,OH}}{K_{O_2}} = K_{OH} = \frac{[ML_2O_2OHML_2][H^+]}{[ML_2O_2ML_2]}$$

so that the olation reaction of the oxygenated complex can now be independently evaluated for the first time.

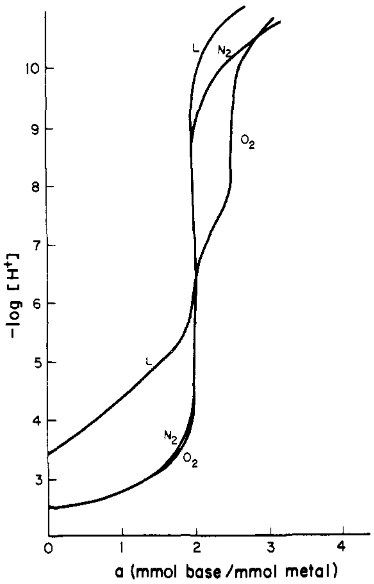

Figure 1. Potentiometric equilibrium curves for the reaction of bipyridine with cobalt at 25.0°, 0.10 M (KNO_3): L = ligand alone; N_2 = ligand in the presence of cobalt in a 2:1 molar ratio, under inert atmosphere; O_2 = ligand in the presence of cobalt in a 2:1 molar ratio under oxygen atmosphere.

For the $Co(bpy)_2$ system, the constants are $K_{O_2} = 10^{4.2}$, $K_{O_2,OH} = 10^{-2.6}$, $K_{OH} = 10^{-6.8}$.

The calculated pK for hydrolysis of the cobalt oxygen complex (6.8) is relatively close to the midpoint of the buffer region (7.3) which is offset by the effect of overlapping buffer regions. This seems to be a rather low pK for cobalt hydrolysis, until the Co(III) character of the metal is taken into account, and thus serves as a measure of "cobalt(III) character" in the complex.

Of somewhat more interest is the relative percent of oxygen complexation implied by K_{O_2} and $K_{O_2,OH}$. Throughout the low pH buffer region a constant amount of oxygen is absorbed, corresponding to approximately 6% of the total cobalt, while at pH 8, where the olation reaction predominates, over 50% of the total cobalt is present as the dioxygen complex (for $[Co]_{total} = 10^{-3}$ M). The stability of this complex increases with pH, and it is 100% formed at and about pH 9. Thus, the effect of the hydroxo bridge in "locking in" the dioxygen, thereby shifting the equilibrium in favor of dioxygen complexation, can readily be seen. Similar calculations were not attempted for the phenanthroline complex, as the irreversible reaction to inert Co(III) products proceeds more rapidly, thus decreasing the accuracy of the measurement.

Initially, the precise nature of this conversion was uncertain. In the course of the irreversible oxidation, for both $Co(bpy)_2$ and $Co(phen)_2$, the initial brown dioxygen complex fades, giving rise to a new yellow species, which is then slowly converted to a final red product. Spectral data for these complexes are summarized in Table I.

Although the initial brown → yellow conversion is accelerated at higher pH, potentiometric data show there is no stoichiometric involvement of OH^- ion in the yellow → red conversion. As the interconversion between yellow and red species does not appear to involve any net hydrolytic reactions, the possibility of geometrical isomerism must be considered. A similar kinetic phenomenon has been observed by Gillard in the geometrical interconversions of some Co(III) complexes.[9]

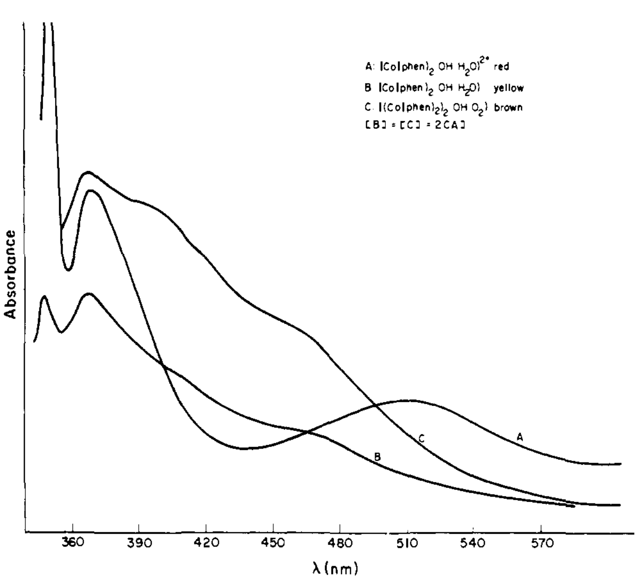

Figure 2. Difference spectra of A, $[(Co(phen)_2O_2OH]^{2+}$ (red); B, $[(Co(phen)_2OHH_2O]^{2+}$ (yellow); and C, $[(Co(phen)_2)_2O_2OH]^{3+}$ (brown) vs. (phen H)$^+$. $T = 25.0°$, $\mu = 0.10$ M (KNO_3).

Since it is now demonstrated that the dioxygen complex involves μ-peroxo-μ-hydroxo bridging, in an obligatory cis geometry, loss of peroxide in going to an inert Co(III) complex should initially result in a cis complex, which can rearrange (in a slower step) to give the final product, *trans*-(Co(phen)$_2$(OH)H$_2$O). This possibility has been proved spectrally (Figure 2). Note the similarity in the spectra of the cis dioxygen complex, and the initial (yellow) oxidation product, which shows two overlapping (λ_{max} ~460, 370 nm) fairly high intensity bands, plus a L → M charge transfer band (λ_{max} 390 nm) in the dioxygen complex. The final pink product, on the other hand, exhibits well-separated bands, at 510 and 370 nm, respectively, with much lower extinction coefficients. (A third sharp band at 350 nm has been observed—for which no assignment is presently made.)

This is precisely what would be expected for the geometrical isomerism proposed. Using octahedral symmetry labels for clarity, the two bands may be assigned as the tetragonal components of the $^1A_1 \rightarrow {}^1T_1$ transition. The trans complex, which has an effective center of symmetry, would be expected to be more Laporte forbidden, thus the lower extinction coefficient of the red complex. Similarly, in the cis (yellow) complex, the average environments of the axes are much more similar than in the trans; thus the tetragonal splitting should be much smaller in the yellow complex than the red, as observed. Therefore we can confidently explain the observed

Table I. Spectral Data for Cobalt Oxygenation and Oxidation Products

Complex	λ_{max}, nm (ϵ)		
$((Co(phen)_2)_2O_2OH)^{3+}$ [a]	435 (~810)	390 (~1330)	370 (~1330)
$(Co(phen)_2OHH_2O)^{2+}$ (yellow)[a]	470 (~90)	370 (~700)	
$(Co(phen)_2OHH_2O)^{2+}$ (red)[a]	510 (~100)	366 (~400)	
$((Co(bpy)_2)_2O_2OH)^{3+}$	620 (58)	~460 (901)	~390 (1540)
$(\{Co(trpy)(phen)\}_2O_2)^{4+}$ [b]	470(6200)	390 (10100)	

[a] Difference spectra vs. *o*-phenanthroline hydrochloride. [b] Reference 4.

conversions as follows. In the brown complex the peroxo- and hydroxo-bridging ligands must occupy cis positions on the metal ion, thus forcing the two *o*-phenanthroline ligands into cis positions. As the peroxo bridge is lost, the yellow, hydrolyzed form of the kinetically inert $Co^{III}L_2$ will at first retain the cis configuration. Over a period of days, the thermodynamically favored, square planar or trans form (red) will slowly be formed. This step should be irreversible, in agreement with the behavior described above. Diagramatically:

$$2Co(phen)_2{}^{2+} + O_2 \rightleftharpoons \underset{\text{brown}}{[(Co(phen)_2)_2O_2OH]^{3+}} + H^+$$

$$\underset{\text{brown}}{[(Co(phen)_2)_2O_2OH]^{3+}} \rightarrow \underset{\text{yellow}}{2\textit{cis}\text{-}[Co(phen)_2(OH)H_2O]^{2+}} + H^+ \text{ (+ peroxo reaction product)}$$

$$\underset{\text{yellow}}{\textit{cis}\text{-}[Co(phen)_2(OH)H_2O]^{2+}} \rightleftharpoons \underset{\text{red}}{\textit{trans}\text{-}[Co(phen)_2(OH)H_2O]^{2+}}$$

The ultimate fate of the peroxo product in the brown to yellow conversion remains unknown. The fact that the complex geometry is preserved in going from the brown to the yellow complex implies that if a simple peroxide dissociation is operative in the oxidation, then the incoming water may become strongly associated in the outer sphere prior to dissociation, and the reaction proceeds through a square pyramidal intermediate with no conversion to a trigonal bipyramidal complex. Alternatively, the reaction may proceed through direct reduction of bound peroxide to water, possibly utilizing another molecule of the dioxygen complex. In this case the initial geometry of the complex must be preserved. This mechanism is inconsistent, however, with the observed pH changes. Insufficient kinetic data are presently available to completely establish the precise mechanism of oxidation.

In the course of our spectral measurements, it was found that the π–π^* band of *o*-phenanthroline at ~270 nm served as a very sensitive indicator of the electronic environment at the phenanthroline nitrogen. Thus, the fully deprotonated ligand absorbs at 262 nm, while the monoprotonated form, with a higher positive charge density at the pyridyl nitrogens, shifts λ_{max} to 270 nm. Further increasing the charge density (in *o*-phen$H_2{}^{2+}$) results in a shift to 279 nm. It was therefore felt that the magnitude of this bathochromic shift could serve as a sensitive measure of the charge density on the cobalt during oxygenation and oxidation. The results of such a study are summarized in Figure 3. The observed charge density produced by the positive metal ions generally follows the expected trend: $Zn^{2+} < Co^{2+} < Cu^{2+} < H^+ < Co^{3+} < 2(H)^+$.

It can be further seen that the charge density produced by the metal ion depends not only on its formal oxidation state but also on its formal charge; e.g., $\lambda_{max}[Co(phen)_3]^{3+}$ 277 nm > $\lambda_{max}[Co(phen)_2OHH_2O]^{2+}$ 271 nm. (It should be noted that $Co(phen)_3{}^{3+}$ exhibits strong "exciton coupling", caused by preferential alignment of the phenanthroline dipoles, which results in a doublet at 274 and 280 nm. For comparative purposes, an average of 277 nm has been used.) This strong effect of formal charge has previously been ignored in phenanthroline band assignments based on "center of gravity" methods,[10] where, for example, the peak maximum of the π–π^* phenanthroline band in $Co(phen)_2$ oxalate is compared to that in $Co(phen)_3$. The present results strongly indicate that in using such methods, only complexes of the same formal charge should be compared.

The most striking result of the phenanthroline study, however, is the position of the bands for the dioxygen complexes. For $[(Co(phen)_2)_2O_2OH]^{3+}$, λ_{max} is 268 nm, precisely the position of the band for $[Co(phen)_2)H_2O)_2]^{2+}$. This was initially quite puzzling, as it seems to imply minimal Co(III) character at the central metal as reflected in the charge density on the pyridyl nitrogen atoms.

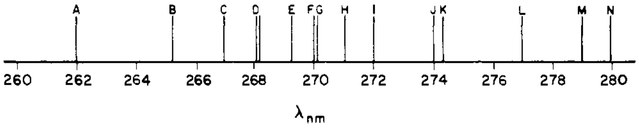

Figure 3. Correlation diagram of effective charge density on the pyridyl nitrogen as a function of coordination environment, as reflected in the π–π^* *o*-phenanthroline (phen) band at ca. 270 nm: A, phen; B, $[Zn(phen)_3]^{2+}$; C, $[Co(phen)_3]^{2+}$; D, $[Co(phen)_2(H_2O)_2]^{2+}$, $[(Co(phen)_2)_2O_2OH]^{3+}$; E, $[Cu(phen)_2]^{2+}$; F, phenH^+ $[HL^+]$; G, $[(Co(trpy)phen)_2O_2]^{4+}$ (peroxide); H, $[Co(phen)_2OHH_2O]^{2+}$ (cis and trans); I, $[Co(trpy)(phen)]^{3+}$; J, $[Co(phen)_3]^{3+}$ high energy exciton band; K, $[(Co(trpy)(phen))_2O_2]^{5+}$ (superoxide); L, $(Co(phen)_3)^{3+}$ average energy; M, phen$H_2{}^{2+}$ (H_2L^{2+}); N, $(Co(phen)_3)^{3+}$, low energy exciton band.

Again, however, the effect of formal charge must be remembered. In the formally Co(III) dioxygen complex, the oxygen moiety is reduced to peroxide; thus each cobalt is subjected to the effect of an additional negative charge. This effect may in itself explain the apparent discrepancy. Other plausible, although more complex explanations involve the nature of the peroxide ligand. The four electrons in the π^* antibonding molecular orbital of $O_2{}^{2-}$ may promote the transfer of electron density into unoccupied d orbitals on the Co(III), thus reducing the positive charge density of the metal ion below that expected on the basis of the electrostatic effect alone. Alternatively, the antibonding electrons on the peroxo ion may overlap to some extent with the phenanthroline ring system itself and add electron density to the ring directly. Either of these effects would move the transition to a higher energy than that for the hydroxo-bonded yellow and red forms of $Co^{III}L_2$, in agreement with observations. Although this explanation has the rather attractive feature of explaining the unusual stability of the terpyridyl-*o*-phen mixed ligand complex, without further evidence for such an interaction, the former explanation must be assumed. While we have been unable to obtain the superoxide $[(Co(phen)_2)_2O_2]^{5+}$, we have investigated $[(Co(phen)(trpy))_2O_2]^{5+}$ which can be obtained facilely by oxidation of the peroxo complex with Ce^{3+} or Cl_2.[4] Here λ_{max} is 270 nm for the peroxo complex, well above that for the simple Co(II) species. The irreversibly oxidized yellow Co(III) products have phen band maxima at 272 nm. Oxidation of the peroxo complex to the superoxo, however, results in λ_{max} 275 nm, higher than that of the simple Co(III) complexes! We have no immediate explanation for this phenomenon, as ESR studies[4] clearly show the odd electron to be localized on the dioxygen rather than the metal, thus implying that the oxygen ligand, rather than the metal, has undergone oxidation.

The results are reminiscent of the suggestion of Werner[11] that the superoxo complex be written $Co^{IV}\text{-}O_2{}^{2-}\text{-}Co^{III}$. While ESR studies obviate this simplistic notion, it may well be that the contribution of this resonance structure is more important than previously recognized; that is, forms A and D may con-

$$\begin{tikzcd}
Co^{IV}\text{-}O_2^{2-}\text{-}Co^{III} \arrow[r, leftrightarrow] & Co^{III}O_2^{-}\text{-}Co^{III} \arrow[r, leftrightarrow] & Co^{III}\text{-}O_2^{2-}\text{-}Co^{IV} \\
\text{A} & \text{B} \arrow[d, leftrightarrow] & \text{D} \\
 & Co^{II}\text{-}O_2\text{-}Co^{III} & \\
 & \text{C} \arrow[d, leftrightarrow] & \\
 & Co^{III}\text{-}O_2\text{-}Co^{II} & \\
 & \text{E} &
\end{tikzcd}$$

tribute significantly to the stabilization of the complex. Alternatively, one can ignore rigorous assignment of formal oxidation states for the metal, and simply assume that the oxidation state is a property of the complex as a whole.

Finally, although less likely, is the possibility that the bridging superoxide may accept π electron density from the pyridyl ring, resulting in increased charge density at the nitrogen.

The similarity in spectra of the protonated ligand and metal ligand complex can be used to advantage in interpretation of d-d spectra. Normally, the strong π-π^* bands of phenanthroline obscure d-d bands below 400 nm. However, using the protonated ligand in the reference cell allows one to obtain a "difference spectra" which is free of ligand bands above 350 nm. This technique was used to obtain the d-d spectra in Figure 2. The difference spectra as obtained by the method described could further be used to calculate ligand field parameters for the oxygenated complex. Normally, the high energy L → M charge transfer band (λ_{max} ~350 for dioxygen complexes of cobalt aliphatic polyamines) obscures all spectral details below 400 nm in the peroxo complexes, making band assignments quite tenuous.

For the condensed pyridyl ligands, however, the charge transfer band is shifted to ~390 nm, consistent with the poorer σ donor properties of the pyridyl nitrogens. (For a L → M charge transfer, the energy should increase as the ligands donate more σ electron density to the metal, thus increasing the energy required for the transfer of charge to occur.) This shift, coupled with the difference spectra technique, enables resolution of the tetragonal component at ~367 nm in the $[Co(phen)_2]_2O_2OH$ complex. Thus the energy of the $^1A \rightarrow {}^1T$ transition can be approximately assigned as the arithmetic average of the tetragonal components (462, 367 nm), and $\Delta E_{^1A \rightarrow {}^1T} \simeq 24\,040$ cm^{-1}.

Using the equations of Lever[12] $\Delta E = 100g + C - 80B^2/10Dq$. Without another band, which cannot be effectively resolved in this system, B cannot be obtained. However, for such a high field $Dq/B > 4$, and, taking $C = 4B$,[12] $\Delta E \simeq 10Dq$. Thus $10Dq \simeq 2040$ cm^{-1} = $[2Dq(\text{phen}) + Dq(\text{OH}) + Dq(O_2^{2-})]$. Using the tabulated values of Figgis[13] for phen ($Dq = 8930$ cm^{-1}) and OH^- (2976 cm^{-1}), $DqO_2^{2-} \simeq 3200$ cm^{-1}. Thus the ligand field strength of "μ-peroxo" dioxygen is slightly higher than that of H_2O. This result is close to that obtained by Gray and Treitel[14] for $(Co(NH_3)_5)_2O_2$ thus supporting their result, and is fully consistent with the chemistry of peroxide, which is a fairly weak σ-donor, and cannot act as a π-acceptor, as its π^* orbitals are filled.

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References and Notes

(1) (a) This work was supported by a research grant, No. GP-43752, from the National Science Foundation. (b) Texas A&M University Health Fellow. (c) Professor of Chemistry, University of Hartford, Hartford, Conn.; Visiting Professor of Chemistry, Texas A&M University, 1974–1975.

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Infrared Spectral Studies of Metal Binding Effects on the Secondary Structure of Bean Plastocyanin

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Abstract: The infrared spectra (4000–200 cm^{-1}) of holo-, apo-, cobalt(II)-substituted, and heat- and acid-denatured bean plastocyanins (*Phaseolus vulgaris*) are assigned. Bands at 1260 and 370 cm^{-1} in apoplastocyanin are shown to be dependent upon secondary conformation and are assigned to an α-helix structure by comparison to homopolypeptide vibrational spectra and analysis of the ultraviolet circular dichroism spectrum of the holoprotein. Further, shifts upon metal incorporation to ~1245 and 345 cm^{-1}, respectively, suggest a metal-associated distortion of the helix to a more extended form. The ir data confirm that cobalt(II) substitutes at the copper site in bean plastocyanin. Based on all available vibrational spectral results, it is proposed that the metal ion is bound to a peptide linkage, which itself is part of a short section of helix present in the protein. There is no effect on this helical section of the site upon reduction of the holoprotein to its copper(I) form.

Recent x-ray photoelectron spectral (XPS) studies have shown[1] that copper is bound to a sulfur atom in plastocyanin isolated from French bean leaves (*Phaseolus vulgaris*). It has also been observed[2] in Raman spectroscopic experiments on the spinach protein that certain amide vibrations are resonance-enhanced, possibly as a result of association of copper with a side chain or a peptide linkage of the plastocyanin backbone. With the goal of learning more about the protein environment in the vicinity of the metal site, we have made a detailed study of the infrared spectra of bean plastocyanin and several of its derivatives.

Experimental Section

Solutions of holo-, reduced, apo-, and cobalt(II)-substituted bean plastocyanins were prepared as described previously.[3] The buffer was removed from the solutions by anaerobic dialysis at 4° against triply