A Theoretical Analysis of Corrin Optical Spectra[1]

Peter O'Donnell Offenhartz, Barbara Hopf Offenhartz,[2] and Mayme Mei Fung

Contribution from the Departments of Chemistry, University of Colorado,
Boulder, Colorado 80302, Amherst College, Amherst, Massachusetts 01002,
and Mount Holyoke College, South Hadley, Massachusetts 01075.
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Abstract: The visible and ultraviolet spectra of a number of corrins, including vitamin B_{12} and the B_{12} coenzyme, are analyzed using simple molecular orbital models. The spectra are interpreted in terms of the net charge on the cobalt atom which resides in the center of the corrin ring. This charge is related in turn to the electron-donating power of ligands bound in the two remaining coordination positions of the metal. It is demonstrated that a single ordering of the ligands can explain nmr chemical shifts and metal-bound CN^- stretching frequencies as well as the optical spectra. A new interpretation of the spectra is used in obtaining this agreement.

The electronic spectra of corrins arise primarily or entirely in the conjugated organic ring system of the molecule.[3-5] Corrins resemble porphyrins in that they contain four pyrrole rings; in corrins, however, the rings are saturated except at the nitrogens and nearest-neighbor carbon atoms, and in addition the conjugation is not fully cyclic owing to the absence of one of the four methene bridges. The basic corrin structure is shown in Figure 1; the conjugated portion has been emphasized with dark lines.

The naturally occurring corrins usually contain cobalt at the center of the ring system; artificial corrins containing cobalt, nickel, and zinc have been synthesized.[6-9] Metal-free corrins also occur in nature,[10] and in addition have been prepared synthetically.[8,9] The cobalt corrins are especially interesting since one can substitute a variety of ligands on the metal above and below the corrin plane;[11-22] these ligands include a number of alkyl groups. In the *cobalamins* (or, equivalently, *cobamides*), a side chain containing a nucleotide terminates in 5,6-dimethylbenziminazole (or a related base) which is bound to tripositive cobalt; the opposing ligand X may vary. Vitamin B_{12} is cyanocobalamin, *i.e.*, $X = CN^-$; the cobalamin coenzyme (DBC) has X = 5′-deoxyadenosine. In the *cobinamides*, the nucleotide is absent, and two replaceable ligands, which we call X and Y, are bound to the cobalt. An additional ligand can *displace* the benziminazole (abbreviated Bz) in the cobalamins, giving rise to compounds such as dicyanocobalamin, in which $X = Y = CN^-$. There is also good evidence for five-coordinate corrin complexes,[16,17] in which the Y position is empty.

The cobalt corrins mentioned above differ only in the nature of the ligands bound to the metal. It is therefore to be expected that all such corrins should have nearly the same optical absorption spectrum, since the conjugated system responsible for the absorption should be only indirectly affected by these changes. Contrary to this naive hope, the cobalt corrin spectra span a number of distinctly different types. It is the main purpose of this paper to classify and interpret these types of spectra.

Many other variations on the basic corrin structure have been studied experimentally. The synthetic corrins prepared by Eschenmoser and coworkers[6,8,9] generally differ from the basic type outlined in Figure 1 in that a cyanide group replaces the hydrogen atom at C(15). This substitution enlarges the π-electron system, thereby changing the fundamental nature of the conjugated system, introducing as well a large asymmetry. Nevertheless, the CN-substituted corrins have spectra similar to the naturally occurring corrins, and, as expected, in those cases where the side-chain cyanide has been removed from the corrin,[7] the artificial compound is found to have a spectrum very similar to the corresponding natural compound.

The cobaltic ion in corrins can be reduced[21,23,24] to both Co^{2+} and Co^{+}, with the reduction accompanied by considerable changes in the spectrum. We are therefore faced with a variety of ways of perturbing the basic corrin electronic structure: (1) replacement of the cobalt by other metals, (2) replacement of one or both of the ligands on the metal, (3) oxidation or reduction of the central metal ion, and (4) substitution on the conjugated ring C(15). As we will show, the spectra

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[2] Author to whom inquiries should be addressed at Mount Holyoke College.

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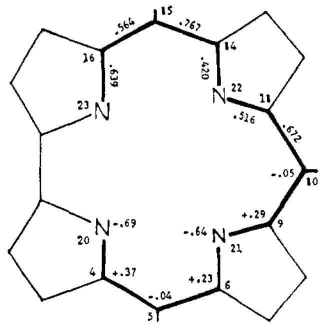

Figure 1. Corrin ring system, with charge densities and bond orders as calculated for a dipositive metal ion.

of many of the different possible compounds can be interpreted in terms of a reasonably simple molecular orbital model. This we do in the next section. Following that, the predictions of a more detailed model, based on the Pariser–Parr–Pople scheme, are examined and are correlated with a wide variety of experimental data, including optical spectra, chemical shifts in the nmr, carbon–cobalt bond strengths, and the metal-bound cyanide stretching frequency. The experimental data on the synthetic corrins are discussed next. Finally, in conclusion, we discuss the theoretical and experimental connections between structure and spectra.

A Simple Theoretical Model

The classical corrin spectrum is that of dicyanocobinamide, given in Figure 2. The main features are a pair of overlapping bands in the visible region of the spectrum in the neighborhood of 550 nm, a very weak but distinct peak near 420 nm, followed by a strong and narrow peak at about 370 nm. The classical spectrum resembles the typical metal porphyrin spectrum, which has a series of bands in the visible beginning (on the long wavelength side) at about 580 nm, followed by a very intense and narrow band in the ultraviolet at about 420 nm. This latter band is known as the Soret. However, the porphyrin spectra are far more intense, with the Soret having an extinction coefficient $\epsilon \sim 3 \times 10^5$. The corresponding ultraviolet band in dicyanocobinamide is weaker by about a factor of 10. On the other hand, the bands in the visible are about of equal intensity in the two classes of compounds, with $\epsilon \sim 2 \times 10^4$, implying, of course, that the ratio of intensity in the ultraviolet to intensity in the visible is often near 20 in the porphyrins, but rarely exceeds 2 in the corrins.

Abridged patterns of π molecular orbitals in both porphyrins and corrins are given in Figure 3. The observed spectra presumably arise from excitations from the highest occupied molecular orbitals (a_{1u} and a_{2u}; ϵ_6 and ϵ_7) to the lowest empty molecular orbitals (e_g; ϵ_8 and ϵ_9). In porphyrins the latter orbitals are doubly degenerate, so the excitations give rise to only two distinct bands. Furthermore, since the highest occupied orbitals are also nearly (but accidentally) degenerate, the two bands interact strongly to produce a high-energy band of high intensity (the Soret) and a low-energy band of low intensity—in fact the visible porphyrin bands would have zero intensity if the highest occupied molecular orbitals were of the right energy to produce degenerate zero-order configurations.[25] In the corrins, on the other hand, the lowest energy excitation ($7 \rightarrow 8$) is nondegenerate, while the next two excitations ($7 \rightarrow 9$ and $6 \rightarrow 8$) may well be nearly degenerate.[26] The final band ($6 \rightarrow 9$) occurs at higher energies and will be ignored for the present. Thus, in a superficial sense, there may be a resemblance between the theory of corrin and porphyrin spectra, in that interactions between degenerate bands may be involved in both, but the resulting porphyrin bands retain a twofold degeneracy arising in the fourfold symmetry of the porphyrin molecule. Furthermore, the interacting corrin bands are preceded by a nondegenerate band at lower energies.

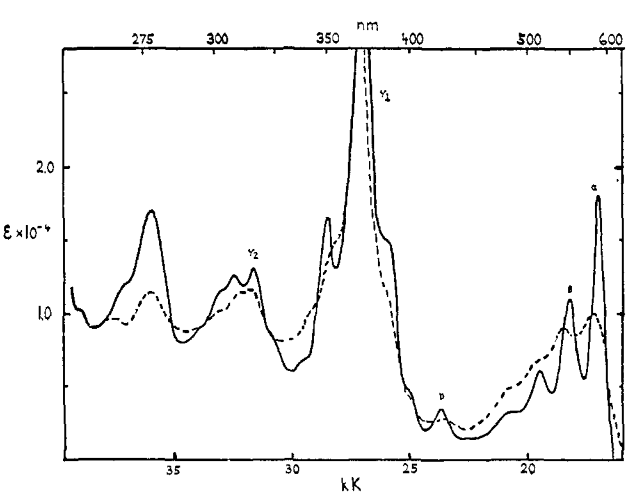

Figure 2. Absorption spectrum of dicyanocobinamide in ethanol at −180° (——)[5,17] and in water at room temperature (- - - -), pH 7.

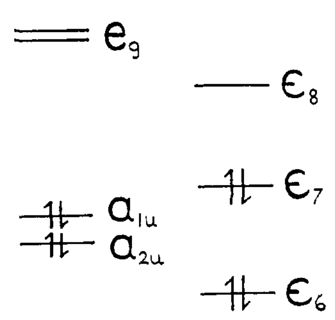

Figure 3. Schematic orbital energy patterns for porphyrins (left) and corrins (right).

Let us for the moment ignore the nondegenerate ($7 \rightarrow 8$) band, which simple calculations and group-theoretical considerations show to be x-polarized, and concentrate our attention on the two near-degenerate transitions ($7 \rightarrow 9$ and $6 \rightarrow 8$), both of which are y-polarized. Let us assume that in the absence of any configuration interaction these two transitions have exactly the same transition dipole moment. (Hückel and PPP calculations bear out this assumption with remarkable consistency; this equality is expected theoretically for alternant hydrocarbons.) If we call the state functions corresponding to these two transitions $\Psi_{7\rightarrow 9}$ and

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(25) M. Gouterman, *J. Mol. Spectrosc.*, **6**, 138 (1961).

(26) The 13 atoms of the conjugated portion of the corrin system hold a total of 14 electrons, giving the corrin ring a net negative charge. There are thus seven doubly occupied molecular orbitals, and the notation $7 \rightarrow 8$ represents a transition from the highest occupied to the lowest empty orbital.

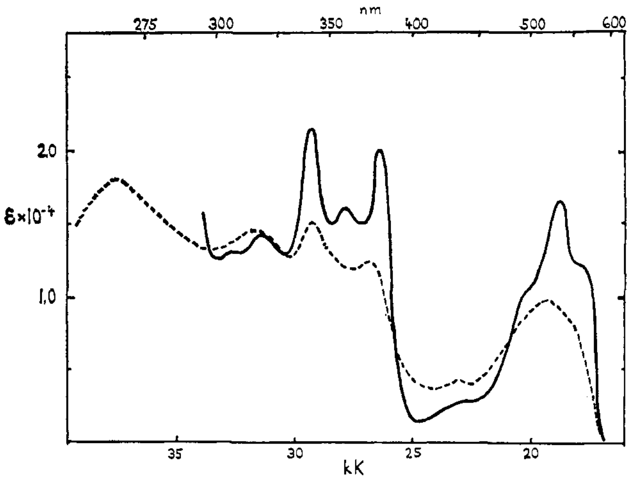

Figure 4. Absorption spectrum of methylcobalamin in ethanol at −180° (—)[5] and in water at room temperature (- - - - -).[35]

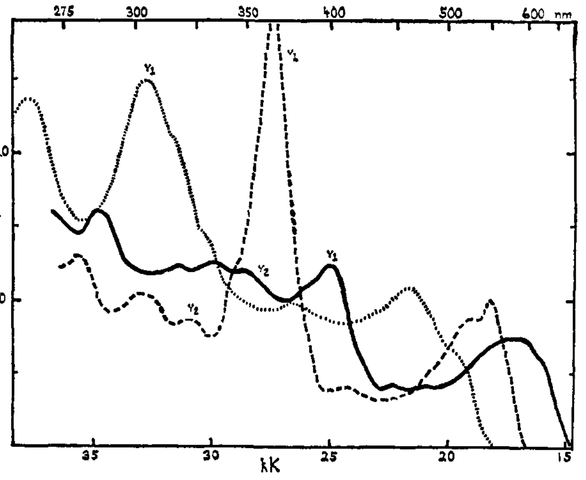

Figure 5. Absorption spectra in water at room temperature of cyanomethylcobinamide (—),[29,35] cyanocobalamin (- - - -), and methylcobinamide (· · · · · ·).[29,35] The spectrum of Co^{2+} cobinamide is very similar to that of methylcobinamide, which is presumably five coordinate.

$\Psi_{6\rightarrow8}$, and the ground state function Ψ_{GS}, then mathematically

$$\langle\Psi_{GS}|\boldsymbol{\mu}|\Psi_{7\rightarrow9}\rangle = \langle\Psi_{GS}|\boldsymbol{\mu}|\Psi_{6\rightarrow8}\rangle \tag{1}$$

where $\boldsymbol{\mu}$ is the dipole moment operator. If the two functions are nearly degenerate any off-diagonal element between them will cause them to couple into two new states which are approximately given by

$$\begin{aligned}\Psi_s &= 2^{-1/2}(\Psi_{6\rightarrow8} + \Psi_{7\rightarrow9})\\ \Psi_w &= 2^{-1/2}(\Psi_{6\rightarrow8} - \Psi_{7\rightarrow9})\end{aligned} \tag{2}$$

Let us call the off-diagonal element Q. Then Ψ_s and Ψ_w will be the correct forms of the new states in the limit that the magnitude of Q is much larger than the separation in energy ΔE between the two original states

$$\begin{aligned}\Delta E &= \langle\Psi_{6\rightarrow8}|\mathcal{H}|\Psi_{6\rightarrow8}\rangle - \langle\Psi_{7\rightarrow9}|\mathcal{H}|\Psi_{7\rightarrow9}\rangle\\ Q &= \langle\Psi_{6\rightarrow8}|\mathcal{H}|\Psi_{7\rightarrow9}\rangle\end{aligned} \tag{3}$$

If Q is negative, Ψ_s will be the lower and Ψ_w the higher in energy of the two resulting states. The reverse applies if Q is positive. In both cases the transition to Ψ_w will have essentially zero transition dipole moment while the transition to Ψ_s will have a substantial intensity. A relationship between Q and the actual intensities I_1 and I_2 is easily derived, and we find

$$\begin{aligned}\frac{2Q}{\Delta E} &= \frac{m}{(1 - m^2)^{1/2}}\\ m &= \frac{I_2 - I_1}{I_1 + I_2}\end{aligned} \tag{4}$$

In the porphyrins, it is found experimentally that the quantity corresponding to our Q is of the order 4 kK (1 kK = 1000 cm^{-1}) while that corresponding to ΔE is generally less than 2 kK. In this way Gouterman[25] has explained the astonishingly large ratio of the Soret band intensity to the visible band intensity. In the corrins, on the other hand, we believe that the magnitude of Q is not nearly so large compared to ΔE, and that it may be variously positive, negative, or close to zero depending on the specific nature of the corrin. In this way we attempt to explain the sensitivity of corrin spectra to minor perturbations, and the comparative insensitivity of porphyrin spectra to similar influences.

Looking at the dicyanocobinamide spectra in Figure 2, it is tempting to make the following interpretation.[3-5] First, the so-called α band near 580 nm is clearly the 0–0 vibrational component of the nondegenerate transition (7 → 8). The β band (first band after the α) and the slow tailing off at higher energies represent the 0–1 and higher vibrational overtones, respectively; this is most clearly seen in the low-temperature spectrum. The D band at about 420 nm, found in nearly all corrin spectra, is *apparently* too far from the α band to be interpreted as another vibrational overtone. We could therefore interpret it as the low-energy component Ψ_w of eq 2, assuming Q appropriately positive. The so-called γ band (the first strong peak in the ultraviolet) would then correspond to Ψ_s.

This, the usual interpretation,[3-5] is not consistent with a great deal of corrin spectroscopy. It does not seem to be consistent with the spectrum of methylcobalamin in Figure 4, which does not show the usual high-intensity γ band, but rather two components of similar intensity, γ_1 and γ_2, while the D band near 420 nm persists. An even wider spread of spectral types is shown in Figure 5. In fact, examining the spectra of vitamin B_{12} and dicyanocobinamide, we note a second band at 300–320 nm which seems to correspond to the high-energy γ_2 peak occurring at 320–350 nm in cyanomethylcobinamide. This peak occurs too low in energy to be interpreted as the 6 → 9 transition, at least according to PPP theory, *vide infra*, and may best be explained as the low-intensity component resulting from the mixture of states $\Psi_{6\rightarrow8}$ and $\Psi_{7\rightarrow9}$. This interpretation requires a *negative* Q for vitamin B_{12}.

If Q is negative, the D band near 420 nm is not as easily assigned. If the band is not associated with either the 6 → 8 or 7 → 9 transition, several other possibilities for its origin may be spin-forbidden singlet–triplet absorption, n–π^* transitions, or metal–ligand charge transfer. Each may be ruled out on elementary grounds. Singlet–triplet transitions ought to be far weaker than the band observed, and, in any event, the band is not enhanced by methyl iodide.[5] Metal–ligand charge transfer is not the source of the band since it is equally prominent in metal-free corrins.[10] Similarly, the energy of n–π^* transitions should depend on the presence of a metal, and in any case should only occur at far higher energies. As far as we can determine, the only remaining possibility is that the 420-nm band is a vibrational component of the 7 → 8 transition. In vitamin B_{12} the separation between the α band (0–0 vibration component) and the 420-nm band is about 7 kK, and while this seems large for a vibrational component, it is not impossible.[27] Alternatively, the band could be the 0–0 vibrational component of the electronic transition to Ψ_5. This interpretation will be considered in greater detail later.

Additional evidence for the present interpretation of the spectra can be developed by noting some of the predictions of a simple Hückel model. In the elementary scheme developed by B. Offenhartz, the conjugated system is treated as a typical polyene, except that a variable value α_N is used for the nitrogen atoms. In Figure 6 we have graphed the band energies 7 → 8, 6 → 8, 7 → 9, and 6 → 9 as a function of k, where $\alpha_N = \alpha_C + k\beta$. It is customary to take $k = 0.5$ for nitrogen, but in the presence of a charged metal ion k may be much greater, and in fact will depend on the amount of positive charge on the metal. Thus, we expect largest values of k for a corrin with a tripositive metal and no ligands, and smaller values when ligands are attached. In fact, the size of k should be dependent on the extent to which the charge on the metal is neutralized by the ligands.

We have also sketched the dependence of Q on k, using the Nishimoto–Mataga[28] method to evaluate the two-center integrals. (We use Hückel orbitals and energies but include two-electron terms in the configuration interaction.) We note the prediction that Q becomes more negative as the net charge on the metal increases. Elementary Hückel theory therefore predicts a correlation between the magnitude of Q, the position of (say) the α band, and the electron-donating power of the ligands. Fortunately, it is possible to arrange many of the known ligands on corrins into such a series, based on nmr shifts[17] and the stretching frequencies of the CN^- ligand bound to the metal.[16] In order of decreasing electron-donating power we may write

$$CH_3CH_2^- > CH_3^- > CH{\equiv}C^- > CN^- > Bz \sim OH^- > H_2O > \text{nil} \quad (5)$$

Of greater interest is the series appropriate to the combined effect of two ligands

$$(CH_3CH_2^-, CN^-) > (CH_3^-, CN^-) > (CH{\equiv}C^-, CN^-) > (CN^-, CN^-) > (CH_3^-, Bz) > (CH{\equiv}C^-, Bz) > (OH^-, CN^-) > (Bz, CN^-) > (Bz, OH^-) > (Bz, H_2O) > (H_2O, CN^-) > (CH_3^-, \text{nil}) > (CH_3CH_2^-, \text{nil}) \quad (6)$$

There are a few places at which eq 6 is at variance with eq 5, but these minor discrepancies do not affect the general argument that the electron-donating power of the ligands is the primary influence on spectra, stretching frequencies, and nmr shifts.

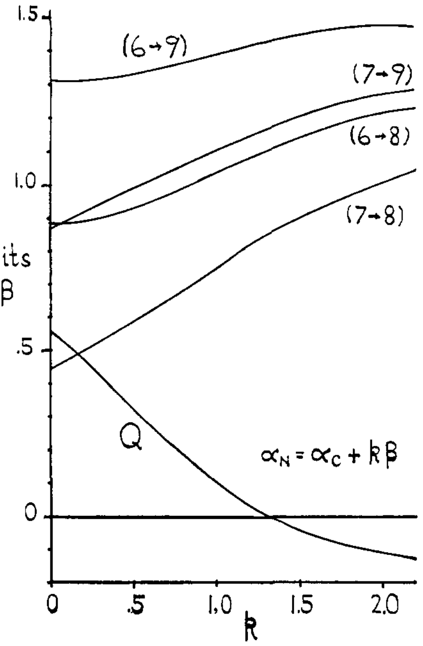

Figure 6. Hückel state energies and the quantity Q (eq 3) as a function of α_N.

The observed spectra[29] follow the predicted trend at least roughly. The complexes formed from a single ligand, with an *empty* coordination position, are shifted furthest to the blue, and show the strongest ultraviolet absorption, indicative of a very negative value of Q. On the other hand, when *two* strongly donating groups are bound to the metal, the absorption is shifted to the red and the ultraviolet spectrum contains two equally strong peaks, indicating a near-zero Q (see Figure 5). However, not all compounds follow this scheme exactly, and a series of closely related corrins may show a small red or blue shift without substantial change in Q, *e.g.*, dicyanocobinamide and cyanocobalamin, or, conversely, minor changes in Q without substantial changes in the position of the α band, *e.g.*, dicyanocobinamide and methylcobalamin. It is to be noted that empirical correlations among spectra, CN^- stretching frequency, and nmr chemical shift were first noted by the Oxford group.[16,17,30,31]

It is interesting to note that the corrin reduction product containing Co^{2+} has a spectrum[32–34] typical of the single-ligand isopropyl–Co^{3+} compound and similar to the five-coordinate methylcobinamide, Figure 5. This implies that Co^{2+} has a net charge on the metal *greater* than that of any observed Co^{3+} compound except the single-ligand complexes. Such a situation is conceivable if the Co^{2+} complexes form very weak and tenuous

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[27] In some porphyrins, both those with and without a central metal, a small peak is found a similar distance from the 0–0 vibrational component of the visible band.

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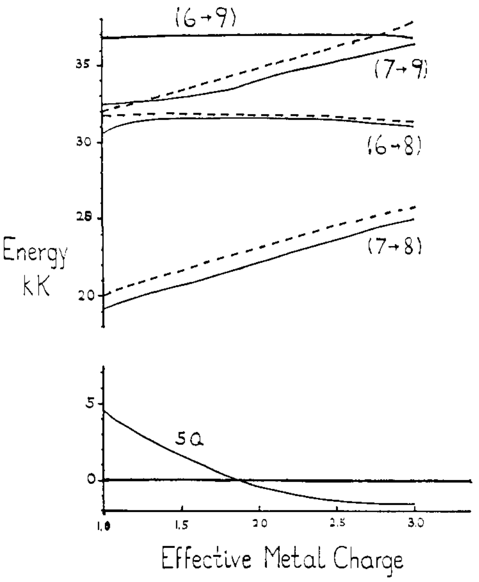

Figure 7. Pariser–Parr–Pople state energies and Q as a function of assumed charge on the central metal ion, both before configuration interaction (----) and after (—).

bonds to the ligands. Since Co^{2+} has an electron in the antibonding d_{z^2} orbital which points at the X and Y ligands, it is entirely likely that it has little affinity for such ligands, and that the metal–ligand bonds which form are longer and less effective in neutralizing metal charge than similar bonds in the Co^{3+} compounds. It is well known that artificial Ni^{2+} complexes, with two electrons in the d_{z^2} orbital, show no ligand affinity. It is also noted that the Co^{+} reduction product[33–35] has a spectrum related to that of cyanomethylcobinamide, in agreement with our theory since Co^{+} has a very low metal charge.

Pariser–Parr–Pople Calculations

In order to test the validity of our simple Hückel model, we have carried out Pariser–Parr–Pople calculations on the corrin system. The results of the calculations are determined by four sets of parameters: the coordinates of the atoms, their valence state ionization potentials, the electron repulsion integrals, and the parameter β. Symmetrized coordinates for corrin are given in Table I; these are chosen so as to preserve the observed bond distances and second-neighbor distances in nickel corrin,[36] but have been averaged so as to give the molecule exact C_{2v} symmetry. Electron repulsion integrals were determined by the Nishimoto–Mataga method,[28] which requires knowledge of the valence state electron affinities. Ionization potentials and electron affinities for carbon were taken as 11.22 and 0.62 eV, respectively, and for nitrogen as 14.51 and 1.20 eV. These are the values used by Weiss and Gouterman[37] in their pioneer calculations on porphyrins. The parameter β was set equal to -2.35 eV throughout all calculations. The metal was taken into account by changing the ionization potentials of all atoms by an amount Ze^2/R_{MX}, where Z is the charge on the metal and R_{MX} is the distance of the metal from the carbon or nitrogen in question. This method is different from that employed by Weiss and Gouterman, but is, we feel, somewhat more consistent with the Nishimoto–Mataga method. The Weiss method gave spectral predictions consistently shifted toward the blue, and Q values consistently more negative than those reported here. Our Q values are indeed insufficiently negative compared with experiments, but on the other hand our spectral predictions are already shifted toward the blue when compared with experiment. We generally included about 13 terms in the final configuration interaction.

Table I. Symmetrized Coordinates (Å) for a Planar Corrin

Atom	x	y	Atom	x	y
N(20)	1.399	1.194	N(23)	1.399	−1.194
C(4)	1.458	2.528	C(16)	1.458	−2.528
C(5)	0.266	3.318	C(15)	0.266	−3.318
C(6)	−0.967	2.795	C(14)	−0.967	−2.795
N(21)	−1.233	1.431	N(22)	−1.233	−1.431
C(9)	−2.605	1.239	C(11)	−2.605	−1.239
C(10)	−3.211	0.000			

Some of the results of the PPP calculations are illustrated in Figure 7. Once again, Q decreases with increasing charge on the metal, passing through zero at about $Z = 1.85$. The energy of the α band increases with increasing metal charge. Contrary to the predictions of simple Hückel theory, the energy of the γ band appears nearly independent of Z, yet, according to our interpretation of the spectra, the γ band follows the α band quite closely. Thus, Hückel results are in somewhat better agreement with our interpretation of the spectra than the PPP calculations. Nevertheless, the confirmation of the trend in Q is encouraging. Note that although PPP theory indicates that at high energies the 6 → 9 band may be observed, its dipole moment is predicted to be much weaker than the dipole of the 6 → 8 or 7 → 9 transition.

The present results may be compared to those of Day,[5] who carried out PPP calculations on corrins as a function of nitrogen electronegativity with emphasis on interpreting the experimental circular dichroism. His results apparently indicated Q always positive, and led him to an ambiguous interpretation of the origin of corrin electronic spectra. As far as we can determine, the reason for his positive Q lies in his neglect of non-nearest-neighbor electron repulsion integrals. The latter approximation cannot be justified on any physical grounds, and indeed does not even make calculations substantially easier. It should not be used merely because it causes little error in certain model examples. Electron repulsion integrals were inadequately considered by Offenhartz[4] and presumably by Kuhn[3] as well, leading in all previous calculations[3–5] to positive Q values.

Unlike previous calculations, our present PPP calculations are able to predict transition energies and intensities consistent with the observed spectra of a large variety of corrin compounds. In the following discussion we will examine the agreement between predicted and observed spectra in greater detail. Problems of spectral interpretation, such as the assignment of band origins, will be considered as well.

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Table II. PPP Values (Å) of the Square of the Transition Dipole Moment M^2

Metal charge, Z	$M_{7\to8}^2$	$M_{6\to8}^2 + M_{7\to9}^2$	$(M_{6\to8}^2 + M_{7\to9}^2)/M_{7\to8}^2$
1.0	1.77	3.76	2.12
1.5	1.54	3.54	2.30
2.0	1.34	3.31	2.47
2.5	1.17	3.10	2.65
3.0	1.00	2.91	2.91

Table III. Gaussian Decomposition of Spectra and Band Assignments

	Transition 7 → 8			Transitions 6 → 8 and 7 → 9				
Compound	No. of gaussians	Energy maxima, k*K*	M^2, Å^2	No. of gaussians	Energy maxima, kK	M^2, Å^2	$(M_{6\to8}^2 + M_{7\to9}^2)/M_{7\to8}^2$	Q, kK
Dicyanocobinamide								
Low-temp	5	17.0–22.6	0.82	11	23.8–34.4	2.00	2.42 (1.98)[a]	−1.0
High-temp	3	17.1–20.4	0.77	8	22.6–34.4	2.14	2.79 (2.05)	−0.7
Methylcobalamin								
Low-temp	3	17.7–20.5	1.04	6	22.8–33.0	2.06	1.97 (1.43)	0.2
Co^{2+} cobinamide	3	19.5–23.0	1.02	4	24.5–31.9	2.53	2.48 (1.78)	<−2.5

[a] Values in parentheses result from reassigning the lowest energy gaussian component(s) of the ultraviolet transitions to the visible (7 → 8) transition; see text.

Calculated band positions are consistently higher in energy than the band origins assigned to the representative spectral types in Figure 5. For example, the α band is predicted to lie between 19 and 25 kK (Z = 1–3), while experimentally the band occurs from 16 to 20 kK. The 6 → 9 transition is predicted at a consistent 37 kK, yet experimental assignments from 35 to 36 kK seem reasonable. The greatest discrepancy shows up with the first γ band. A constant 31 kK is predicted, but a variation of 25–31 kK is observed. Of course, the percentage error is not large. However, even small errors become very important in the calculation of the energies of the 6 → 8 and 7 → 9 transitions, since the predicted spectrum is quite sensitive to the exact value of Q and the separation between the bands.

Theoretical band intensities, given by the square of the transition dipole moment in Table II, are consistent with the band assignments and the intensities summarized in Table III for three spectral types. A spectral decomposition into gaussians was used to measure the absorption intensities in different spectral regions. It was hoped that gaussians would be helpful in resolving vibrational patterns in regions of band overlap and thus help in the assignment of band origins. However, even the low-temperature dicyanocobinamide spectrum in Figure 2, with at least 16 resolvable peaks in the region 15–35 kK, is insufficiently resolved in the ultraviolet to distinguish band origins unequivocably.

While the details of a particular spectrum may be unclear, the study of different spectra may still yield a consistent interpretation. For example, both the predicted and observed band intensities summarized in Tables II and III show only small variations with metal charge. The total absorption assigned to the first three electronic transitions averages 3 Å for the representative spectra in Table III. The PPP calculations, as expected, give results about 70% higher. The intensity of the visible transition is consistently overestimated in the PPP calculations by a similar amount. Note that the *combined* moment $M_{6\to8}^2 + M_{7\to9}^2$ should not depend on the extent of interaction between the two ultraviolet transitions.

Although PPP calculations overestimate absolute intensities, the calculated intensity of the ultraviolet absorption relative to the visible absorption agrees well with the observed ratio. Disagreement here would imply that we have not assigned the experimental bands correctly. The variation in the calculated ratio $(M_{6\to8}^2 + M_{7\to9}^2)/M_{7\to8}^2$ is 2.12–2.91 (Z = 1–3). The observed ratio 2.4 ± 0.4 is in good agreement, provided the D band around 400 nm is assigned to the ultraviolet transition. If the D band is assigned to the visible transition, the observed ratio averages 1.7 (parenthetical values in Table III). The sensitivity of the experimental ratio to the assignment of the weak band is well illustrated by the low-temperature spectrum of dicyanocobinamide. (The high-temperature spectra seem more sensitive to the assignment only because the gaussian chosen to represent the D band contains additional unresolved vibrational components.) The D band corresponds to the gaussian components 5 and 6 at 23.8 and 25.0 kK, respectively. If we assign the 23.8-kK band to the 0–0 vibrational component of the γ_1 band, the ratio is 2.42. If the two gaussians are assigned to the visible transition, the ratio becomes 1.98. The assignment of the D band to the ultraviolet transition is thus somewhat more consistent with the PPP intensity ratios in Table II. However, the disagreement between calculated and observed band position of the γ_1 band would then be even more severe than discussed previously.[38]

Lastly we turn to a comparison of predicted and observed values of Q. From Figure 5 it seems clear that as the corrin spectra shift toward the red, the absorption in the ultraviolet becomes less concentrated in a single peak. According to our interpretation this is because the quantity Q is nearly zero, allowing the two electronic bands to have nearly equal intensity. However, because of the vibrational problem, it is quite difficult to determine the band origin of the second γ band. An estimate of the intensities of the two γ bands is at best semiquantitative. We have estimated Q for dicyanocobinamide from its low-temperature spectrum. If we count the 29.8-kK component as the last vibrational overtone of the γ_1 band, the second band will begin at 30.8 kK, and the ratio of intensities in the two γ bands is then 2.25. With ΔE = 4.6 kK this implies Q = −1.0 kK. This sets an intermediate

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(38) Perhaps we are observing a high-frequency vibrational overtone of the α band which has borrowed intensity from the γ band through vibronic coupling. This interpretation is consistent with the calculated intensity ratios. We are indebted to C. Weiss for pointing this out to us.

value for Q, which is somewhat more negative in compounds such as methylcobinamide and near zero in methylcobalamin. Previous investigators[29] have classified the spectrum of this latter compound as "anomalous", presumably because it is low in intensity in the region around 350 nm and does not resemble the spectrum of vitamin B_{12}. We wish to emphasize that none of the corrin spectra appear anomalous in any gross way, once it is assumed that Q is small and/or negative for all corrins; on the other hand, if a positive Q is assumed, it is difficult indeed to rationalize the γ-band positions and shapes. Estimated experimental values of Q are given in Table III.

Calculated and observed values for other physical properties can be compared as well. Bond orders and charge densities calculated with $Z = 2$ are shown in Figure 1. The correlation between calculated bond orders and observed bond lengths is reasonable. Position C(10) has the greatest negative charge density of any ring carbon atom, with C(5) and C(15) close behind. Experimentally,[15] electrophilic substitution occurs preferentially at C(15), with C(5) somewhat hindered sterically. We are unable to explain why attack at C(10) does not seem to occur.

The PPP calculations also predict that the net charge on C(10) should vary (nearly linearly) from about -0.12 for $Z = 1$ to $+0.01$ for $Z = 3$. This change in net charge will affect the nmr chemical shift of the proton bound to C(10). It is expected that the more negative the carbon atom, the higher the value of τ. Thus, strongly electron-donating ligands should produce high τ values, and this is what is observed.[17,30] Ethyl- and isopropylcobinamides, which have the sixth metal coordination position empty, have the lowest τ (3.0), while dicyanocobinamide has the highest τ (4.2). It is on this basis that the ordering of eq 6 has been established. However, chemical shifts at H(10) for ethylcyanocobinamide, methylcyanocobinamide, and vinylcyanocobinamide have not been measured, and their order was established by considering metal-bound CN^- stretching frequencies; *vide infra.*

Firth, *et al.*,[17] have also established a linear relationship between the H(10) τ value and the wavelength of the β band. (The β band was used rather than the α band in the belief that the intensity of the latter is too variable to locate it as precisely as the former. The separation between the two bands is apparently constant.[29]) This is to be expected on the basis of Figure 7 and our postulated relationship between Z and τ. It is of interest to note that the energy of the β band is 22 kK for methylcobinamide and 18 kK for dicyanocobinamide. According to Figure 7, such a change implies that Z has varied over a range of 1.3 charge units.

Molecular Orbital Mixing of Corrin, Metal, and Ligands

We have argued that many of the physical properties of corrins may be explained on the basis of the net charge on the cobalt ion in the center of the ring system. It is obvious, however, that molecular orbital mixing between the metal, its ligands, and the corrin ring system may have an influence on these properties, if only because the donation of charge takes place *via* this mixing. In unpublished work we have considered this influence in a qualitative way, by taking into account the symmetries of the various orbitals and the degree to which they can be mixed together. We do not wish to draw any final conclusions at this time, since we plan to carry out extended Hückel calculations[39] in which the interactions among corrin, metal, and ligands are considered explicitly. Nevertheless, the qualitative work suggests that corrin–metal–ligand mixing will have little influence on the spectra of the various complexes. Such trends as are predicted on the basis of mixing seem to closely parallel those predicted on the basis of electron-donating power.

Synthetic Corrins

Two kinds of synthetic corrins have been prepared, those with a cyanide group attached to C(15), and those without such a group. The addition of a conjugated group at C(15) completely destroys the approximate C_{2v} symmetry of the corrin, and our preliminary calculations indicate that the trends predicted above for the natural corrins—variation of the band energies and of Q with net metal charge, and so on—need not be true of the special synthetic compounds. For certain specific values of the effective metal charge, the special C(15)–CN compounds may indeed have spectra very similar to the natural corrins, but our preliminary results seem to indicate that for complexes with very highly positively charged metal ions at their center, the spectrum could be dramatically changed. Since Figure 7 no longer applies, we will not discuss the spectra of the special C(15)–CN corrins at this time.

Synthetic corrins without the C(15)–CN have spectra entirely similar to those occurring in nature—at least insofar as they have been studied. The only difference seems to be a fairly uniform shift of the artificial spectra toward shorter wavelengths, amounting to about 1 kK. An excellent graphical comparison is given in Figures 12 and 13 of ref 6. The synthetic cobalt dicyanide complex has β and γ bands at 510 and 349 nm, respectively, compared to 542 and 365 nm for dicyanoheptamethyl cobyrinoate. Similarly, in acid solution, the artificial complex has β and γ bands at 470 and 334 nm, compared to 494 and 353 nm for the natural compound. The shift certainly should not be attributed to a change in the net charge on the metal, if only because the shapes of the two sets of spectra, natural and synthetic, are so nearly identical. The explanation presumably lies in the shape and degree of planarity of the molecules, and perhaps, to a limited extent, in the inductive influence of CH_3 and $CH_2CH_2COOCH_3$ groups on the corrin ring system. It is clear that the difference cannot be due solely to inductive effects, since the spectra of compounds with methyl groups at C(5) and C(15) are little different from compounds with hydrogens at these positions. On the other hand, there is little change in the shape of the vibrational structure, implying little change in the shape of the molecule.

In addition to the above cobalt complexes, Fischli[9] has listed spectral parameters for a synthetic complex of Ni^{2+}; the β band appears at 429 nm, and the γ band at 316 nm. The spectrum is similar to that of natural corrins which have been reduced to Co^{2+}, although shifted even further to the ultraviolet. Presumably this

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(39) M. Zerner, M. Gouterman, and H. Kobayashi, *Theor. Chim. Acta*, 6, 363 (1966).

is indicative of the inability of Ni^{2+} to attract ligands and its consequent very high net charge.

Corrin Structure and Spectra

It is often difficult to properly interpret and assign the spectrum of a given corrin compound. All electronic bands are complicated by the presence of vibrational components, and the intensities of these components are quite variable. Thus, in the ultraviolet, it is difficult to be sure where the first γ band ends and the second begins, and in the visible the α band is often so weak that it is very hard to be sure where the 0–0 assignment should be made. In the present paper, assignments (see Table III) have been as much guided by theory as has the theory itself been guided by experiment. By implication, it is difficult to assign the spectrum of a compound whose structure is unknown.

A major aim of the present study has been to relate structure and spectra in sufficient detail that useful information about the structure of an unknown corrin complex could be obtained from its spectrum. Yet as noted, assignments are difficult to make. We suggest the following guidelines in using an experimental spectrum. (1) The classification scheme of Firth, *et al.* (see Figure 4 of ref 29), is quite useful. (2) The most important feature in the spectrum is probably the position of the β band. Generally speaking, unless a clear and sharp α band can be seen in the spectrum, the β band may be taken as the first distinct but broad band in the visible. (3) The position of the β band is determined by the net charge on the metal, progressing (for naturally occurring Co^{3+} complexes) from nearly 600 nm for the ligand pair (CH_3^-, CN^-) to just above 450 nm for the single-ligand "base off" system with the CH_3^- ligand. The assignment of the β band, although not completely trivial, is less difficult than the assignment of any other band. (4) Since the position of the β band is directly related to the metal charge, reduction of the central metal ion will be important. Co^+ complexes will have spectra well to the red ($\beta \sim 600$ nm); the spectra of Co^{2+} complexes will depend on the donating power of such ligands as may be attached to the metal, but will be generally toward the blue since Co^{2+} forms only weak bonds to its ligands. If *higher* oxidation products of cobalt can be formed, they would have spectra shifted far to the blue. (5) Similar statements can be made concerning the replacement of one metal by another; the oxidation state of the metal and the donating power of the ligands with which it combines will be the primary factors in determining the location of the β band.

Spectra not fitting the pattern of Figure 4 of ref 2 may be caused by oxidation or reduction of the ring system itself, or by the addition of conjugated groups to the ring. It is obvious that reduction of the ring will move the spectrum toward shorter wavelengths.

Possibly the most interesting features of corrin chemistry are the observed equilibrium *trans* effect,[16,18] in which the metal–ligand bond is weakened through donation of charge by a *trans* ligand, and the related formation of a five-coordinate cobalt ion when the *trans* ligand has maximal electron donating power. The equilibrium between five- and six-coordinate species causes the observed spectrum to be temperature dependent, and this dependence provides yet another test of structure.

We have been unable to correlate structure with circular dichroism, or the observed circular dichroism with calculated electronic structures. We suspect that much of the variability of the circular dichroism is due to the influence of vibrational excitations on optical rotation. Until a theory of vibronic influences on circular dichroism is developed, and until the vibronic bands in the corrins are well understood, we see little hope of interpreting the experimental circular dichroism curves.

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