A Study of the Reduced Species of Cobalt and Nickel Complexes Analogous to Vitamin B_{12}

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Abstract: Reduced products of nickel(II) and cobalt(II) 1,19-diethoxycarbonyltetradehydrocorrin cations have been generated by sodium film reduction in THF under high vacuum and studied by optical and esr spectroscopy. Simple one- and two-electron reduction products have been observed in both cases. The one-electron reduction product of the nickel complex is an unusually stable neutral free radical, while that of the cobalt complex is a very stable cobalt(I) species. The two-electron reduction products are both formulated as metal(II) complexes with the two extra electrons located in the ligand π orbitals, thus indicating a unique sequence for the oxidation state of the central cobalt ion of +II → +I → +II on reduction of the parent cobalt complex. The relationships between the electrochemical properties of these complexes and those of analogous corrin systems are also discussed.

The chemistry, and in particular the redox properties, of vitamin B_{12} and its derivatives is a subject of much current interest.[2] Much work has also been carried out on vitamin B_{12} model compounds[3] where it is hoped to gain information which may throw light on the chemistry, electronic structure, redox properties, etc., of the vitamin B_{12} complex itself. These complexes are usually of the cobaloxime type. In this paper we present the results of studies on the reduced species of nickel and cobalt complexes of 1,19-disubstituted tetradehydrocorrins[4] whose ring structures are closely related to the corrin ring of vitamin B_{12}. The structure and numbering of these complexes are shown in Figure 1A, and it is readily appreciated that they are closely related to the corrin ring structure of vitamin B_{12} (Figure 1B) and also the porphyrin and corrole rings (Figures 1C and 1D). Useful comparisons between the properties of the present complexes and those of corrinoids ought to be possible, therefore.

It is now well established that porphyrin and phthalocyanine complexes of closed shell metal ions may be reduced both chemically and electrolytically to give radical anions with extra electrons essentially located in the ligand π orbitals.[5-7] It has also been shown in the case of cobalt(II) complexes of porphyrins and phthalocyanines that a cobalt(I) species is generated initially on reduction.[5c,6-8] Other transition metal ion complexes may also be reduced at the central metal ion rather than the ligand[6,8,9] but in both these cases and that of the cobalt complexes, subsequent ligand reductions are also thought to occur.

In the case of corrinoid complexes, species with the central cobalt ion in the oxidation states +III, +II, and +I have been identified,[2,10,11] but little attention seems to have been given to whether further reduction of the complex is possible and the role of the ligand π orbitals in determining the nature of the reduced species formed. In the subsequent sections we consider these possibilities in the light of the present work.

Experimental Section

The nickel(II) and cobalt(II) 1,19-diethoxycarbonyl-8,12-diethyl-2,3,7,13,17,18-hexamethyltetrahydrocorrins were kindly supplied by Professor A. W. Johnson [University of Sussex, U. K.]. Their preparation and purification have been described in the literature[4] and the samples were used without further purification. The 1,19-ethoxycarbonyl groups are thought to exist in the trans configuration. 1,19-Dimethyl-substituted derivatives are also known. The nickel complex was in the form of a crystalline nitrate, and the cobalt complex a perchlorate.

The reductions were performed in THF solution under high vacuum using metallic sodium as a reducing agent. The sodium metal was deposited as a thin film in one arm of the apparatus by thermal decomposition of sodium azide. THF, which had been purified by repeated vacuum distillation from sodium–anthracene was then distilled into the apparatus, which was then sealed under vacuum. The sample, contained in a second arm of the apparatus, could then be reduced by dissolving it in the THF and washing the solution over the sodium film. The apparatus was designed to allow the measurement of both the electronic and electron spin resonance spectra at the same state of reduction in the absence of sodium metal. The electron spin resonance spectra were recorded on a Varian 4502-15 esr spectrometer fitted with a dual-sample cavity. All the spectra were recorded at X-band frequency, and the spectra were calibrated using either solid DPPH (g = 2.0036) or a solution of Fremy's salt in aqueous potassium hydroxide solution (g = 2.0055, a_N = 13.0 G), together with the field dial of the spectrometer. Measurements at liquid nitrogen temperature (77°K) were made in a quartz dewar. Silica esr tubes were used for all the measurements, and neither these nor the dewar vessel showed any esr signal. A base line drift was observed for the measurements at 77°K due to the high instrument settings required to detect the transition metal ion resonances at the low concentrations (10^{-3} M) used. The low concentrations were dictated by the limited solubility of the complexes in THF. The base line drift does not interfere with the interpretation of the spectra, however.

The electronic spectra were measured using a Beckman DK 2A ratio recording spectrophotometer. Both the parent complexes and the species generated on reduction were studied over the concentration range 5×10^{-5}–1×10^{-3} M. No significant concentration effects were observed for the electronic spectra over this range.

Polarographic measurements on these samples were made by Dr. J. M. Dyke (University of Bristol), using an automatic scanning

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[1] Department of Theoretical Chemistry, University of Sydney, Sydney, 2006, New South Wales, Australia.

[2] H. A. O. Hill, J. M. Pratt, and R. J. P. Williams, *Chem. Brit.*, 5, 156 (1969).

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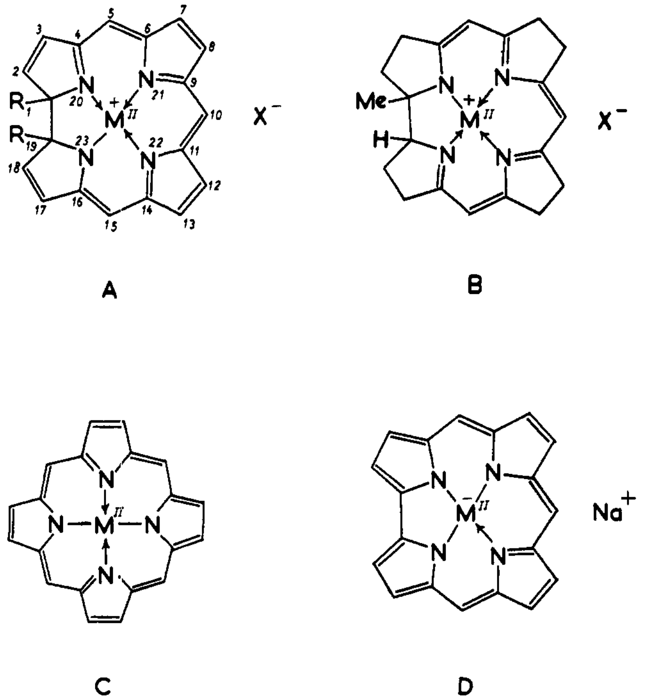

Figure 1. Metal complexes of macrocyclic tetrapyrrole ligands: A, metal(II) 1,19-disubstituted tetradehydrocorrin cation; B, metal(II) corrin cation; C, metal(II) porphyrin; D, metal(II) corrole anion.

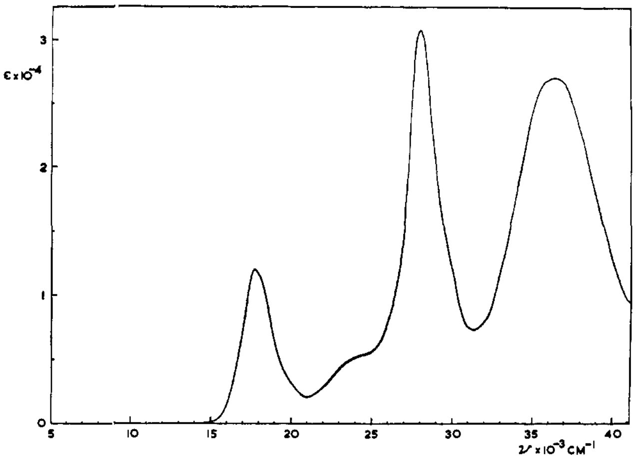

Figure 2. Electronic spectrum of nickel(II) 1,19-diethoxycarbonyl-8,12-diethyl-2,3,7,13,17,18-hexamethyltetradehydrocorrin nitrate in THF.

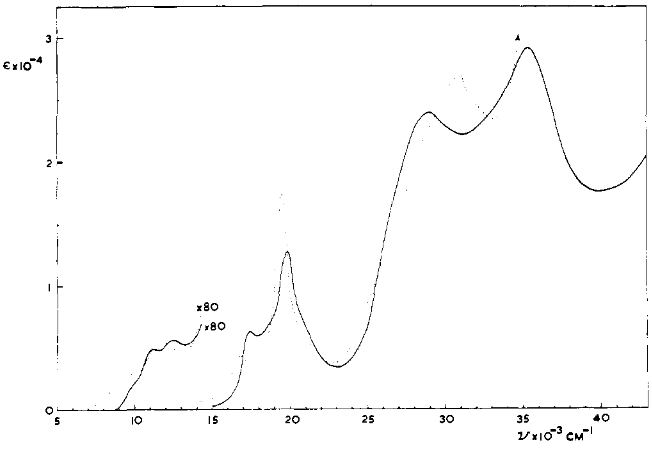

Figure 3. Electronic spectrum of cobalt(II) 1,19-diethoxycarbonyl-8,12-diethyl-2,3,7,13,17,18-hexamethyltetradehydrocorrin perchlorate: (——) in THF; (· · ·) in pyridine.

polarograph, and were carried out in DMF, using tetra-*N*-propylammonium perchlorate supporting electrolyte (0.1 *M*). The same concentrations used were around 5×10^{-4} *M*. Details of the polarographic cell and solvent preparation have been given elsewhere.[5b] Polarographic studies of thallous nitrate showed that the nitrate anion is not reduced under the present experimental conditions and thus should not interfere in the reduction of the nickel–tetradehydrocorrin complex. The polarographic results reported in this paper form part of a broader study of the polarographic behavior of a variety of tetradehydrocorrin complexes which will be reported in greater detail elsewhere.[12]

All reduction potentials quoted in the present paper are with respect to a saturated calomel reference electrode (sce). Other solvents used were commercial samples purified by standard laboratory procedures.

Results and Discussion

A. Parent Complexes. The electronic spectra of the nickel(II) and cobalt(II) 1,19-diethoxycarbonyltetradehydrocorrin complexes are shown in Figures 2 and 3, respectively, and it may be safely assumed that the bands occurring at energies greater than 16,000 cm^{-1} arise from the $\pi \rightarrow \pi^*$ transitions of the ligand as in the case of metal porphyrins[13] and corrins.[14] While broadly similar, there are distinct differences between the two spectra. In the case of the cobalt complex, the absorption in the visible region around 18,000 cm^{-1} appears as two distinct bands, whereas only one is present in the case of the nickel complex. The two main bands in the ultraviolet region are also broadened considerably compared with those of the nickel complex.

No concentration dependence was observed for the spectrum of either complex in THF but the spectrum of the cobalt complex shows an appreciable solvent dependence. The spectra in both THF and pyridine are shown in Figure 3. The spectrum in solvents such as DMF and methanol is intermediate between these two. No solvent dependence was observed for the electronic spectrum of the nickel complex in these solvents.

The solvent dependence in the case of the cobalt(II) complex presumably arises from the differing degrees to which the solvent is capable of further coordinating with the complex in the axial positions. Thus the effect of increasingly strong axial coordination of solvent molecules is to increase the extinction coefficient of the band in the 28,000–31,000-cm^{-1} region and shift it to higher energy. On the other hand, the bands in the visible region tend to shift to slightly lower energy, with the first band decreasing in intensity and the second increasing.

The differences in the electronic spectra of the nickel(II) and cobalt(II) complexes may arise partly from conformational changes of the ligand on changing the central metal ion and also from differences in further axial coordination. The fact that the nickel(II) complex shows no observable change in the electronic spectrum in different solvents suggests that further axial coordination is relatively weak in this case.

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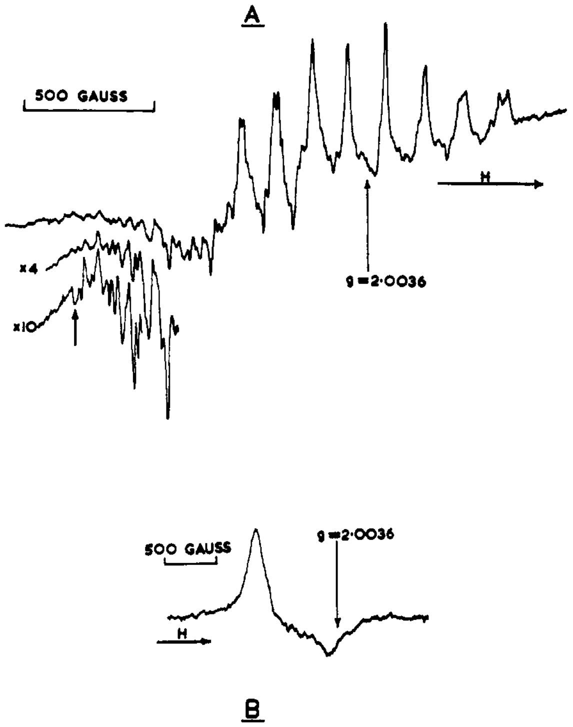

Figure 4. Esr spectrum of cobalt(II) 1,19-diethoxycarbonyl-tetradehydrocorrin perchlorate in THF (10^{-3} *M*): A, at 77°K; B, at room temperature.

However, changes in the electronic structure of the central metal ion should also contribute to the observed spectral differences. Indeed, Firth, *et al.*,[15] have indicated that the observed spectral differences of various vitamin B_{12} derivatives may be considered as arising from combinations of these effects and that changes in the electronic structure of the central metal ion may not be possible without associated conformational changes of the corrin ring.

The weak bands observed below 14,000 cm^{-1} for the cobalt(II) complex, and which are not present in the spectrum of the nickel(II) complex, presumably arise from d–d transitions associated with the central cobalt ion. The nickel(II) complex has been shown to be diamagnetic by nmr measurements[3] and therefore showed no esr signal. The cobalt(II) complex, however, shows a characteristic low-spin cobalt(II) resonance, for which $S = {}^1/_2$. The spectra observed in THF and pyridine at concentrations of 1×10^{-3} *M* are shown in Figures 4 and 5, respectively, and are similar to those observed for various cobalt(II) porphyrins.[16,17] In both cases hyperfine coupling to the central cobalt(II) ion is observed in the frozen solution, but the coupling is not resolved at room temperature, presumably due to line width variation of the hyperfine lines.

In THF, the spectrum at 77°K shows a set of eight hyperfine lines due to interaction with the cobalt nucleus ($I = {}^7/_2$), with a g value close to spin free. At lower fields a complex series of lines is observed, complete analysis of which is extremely difficult. More than one series of hyperfine lines appear to be present, which could arise from the existence of more than one species with slightly different conformations having slightly differing g values and hyperfine couplings, as suggested in the case of cobalt(II) tetraphenylporphine.[16] The complexity could also arise from a small rhombic distortion of the perpendicular g-tensor component; *i.e.*, the g tensor no longer has axial symmetry. It seems that any such rhombic distortion is small, however, and to a reasonably good approximation the esr signal may be assumed to have axial symmetry.

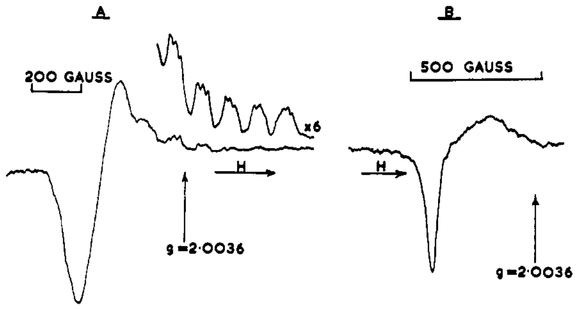

Figure 5. Esr spectrum of cobalt(II) 1,19-diethoxycarbonyl-tetradehydrocorrin perchlorate in pure pyridine (10^{-3} *M*): A, at 77°K; B, at room temperature.

The spectra at 77°K in both THF and pyridine were analyzed in terms of the spin Hamiltonian

$$\mathcal{H}_s = g_{\parallel}\beta_e H_z S_z + g_{\perp}\beta_e(H_x S_x + H_y S_y) + A\cdot S_z I_z + B(S_x I_x + S_y I_y) \quad (1)$$

using the methods of Kneubuhl[18] and Walker,[17] and the g and hyperfine tensor components determined from the experimental spectra are given in Table I. The values of $g_{\perp}$ and B given for the complex in THF correspond to the strongest series of hyperfine lines observed. For the spectrum in pyridine, accurate values of $g_{\perp}$ and B are difficult to obtain due to the broad profile of the low-field absorption. Accurate values may only be obtained by computer simulation of the line shape.[19] We have therefore estimated B from the line width of the perpendicular g-tensor component, and the value quoted for $g_{\perp}$ corresponds to the point where the derivative curve crosses the base line. This should be regarded as a lower limit for $g_{\perp}$.[17] It is also worth noting the change in relative intensities of the $g_{\parallel}$ and $g_{\perp}$ components in THF and pyridine. Such behavior is also observed in the case of cobalt(II) tetraphenylporphines on changing from solvents such as $CHCl_3$ and toluene to pyridine.[16,17]

In pyridine, the parallel cobalt hyperfine lines exhibit a triplet superhyperfine coupling due to the nitrogen of a single pyridine molecule in the axial position, and this is good evidence that the unpaired electron of the cobalt(II) ion is in the d_{z^2} orbital in this particular case.[20,21] While this does not exclude the possibility of weak coordination by solvent molecules in the sixth ligand position, it is interesting to note that a defininte 2:1 pyridine complex is not formed as in the case of cobalt(II) phthalocyanine.[22] Cobalt(II) tetraphenyl-

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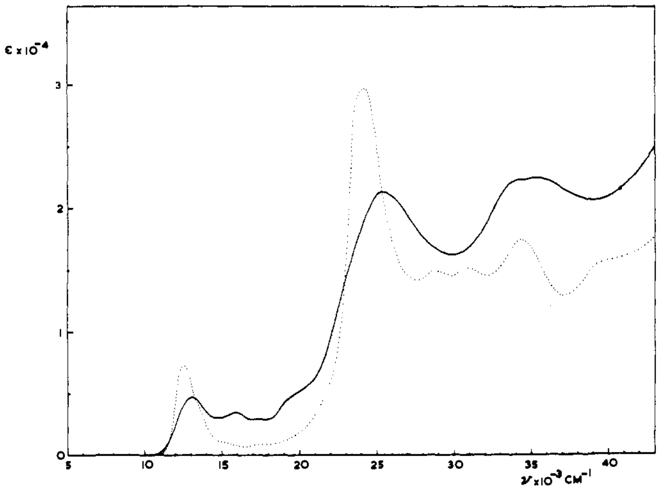

Figure 6. Electronic spectra of the nickel and cobalt 1-ethoxycarbonyltetradehydrocorrin species: A (···), nickel derivative; B (—), cobalt derivative.

porphines have been observed to form both 1:1 and 2:1 adducts with pyridine and other amines in toluene glasses,[17] whereas vitamin B_{12r} and its derivatives usually form 1:1 adducts with such ligands.[20] The behavior of the present complex therefore appears to parallel that of the vitamin B_{12r} derivatives more closely.

Table I. Spin Hamiltonian Parameters

For $[Co^{II}\text{-}1,19\text{-}(CO_2Et)_2Cn]^+ClO_4^-$	
(a) In THF	
At 77°K	$g_\parallel = 1.993 \pm 0.002$ $g_\perp = 2.374 \pm 0.003^a$ $A = 146 \pm 2$ G $B = 80 \pm 2$ G[a]
At room temperature[b]	$g_{iso} = 2.268 \pm 0.010$ $A_{iso} = 97 \pm 6$ G
(b) In pyridine	
At 77°K	$g_\parallel = 1.998 \pm 0.002$ $g_\perp = 2.180 \pm 0.002^c$ $A = 106 \pm 2$ G $B = 33 \pm 9$ G[c] $A^N = 19 \pm 1$ G
At room temperature[b]	$g_{iso} = 2.169 \pm 0.010$ $A_{iso} = 32 \pm 3$ G
For the Second Reduction Product of $[Co^{II}\text{-}1,19\text{-}(CO_2Et)_2Cn]^+ClO_4^-$ in THF at 77°K	
Spectrum 9A[d]	$g_\parallel = 2.042 \pm 0.003$ $g_\perp = 2.438 \pm 0.003$ $A = 118 \pm 5$ G $B = 105 \pm 5$ G
Spectrum 9B	$g_\parallel = 2.003 \pm 0.003$ $g_\perp = 2.461 \pm 0.003^a$ $A = 118 \pm 4$ G $B = 110 \pm 3$ G[a]

[a] Taken for strongest series of hyperfine lines observed. [b] g_{iso} assumed to be midway between maxima of resonance; A_{iso} calculated using maxima as limits of line width. [c] $g_\perp$ taken as the point where the derivative line crosses the base line. B estimated from line width. [d] Difficult to determine $g_\parallel$ and A accurately due to the presence of the radical resonance. The reasons for the differences between g_{iso} and $^1/_3(g_\parallel + 2g_\perp)$, and A_{iso} and $^1/_3(A + 2B)$, for $[Co^{II}\text{-}1,19\text{-}(CO_2Et)_2Cn]^+ClO_4^-$ are given in the text. The esr spectrum of the second reduction product was not observable at room temperature.

The esr spectra of the complex at room temperature do not show any resolved cobalt hyperfine coupling, as mentioned earlier. Again, therefore, it is difficult to obtain accurate values of g_{iso} and A_{iso} without computer simulation of the spectrum. Accordingly, g_{iso} was taken as the midpoint between the maxima of the resonance, and A_{iso} was estimated using the maxima as limits of the liue width. The differences between $^1/_3 \cdot (g_\parallel + 2g_\perp)$ and $^1/_3(A + 2B)$ and the isotropic valnes quoted for the spectra undoubtedly arise from the difficulties in estimating the latter, and also $g_\perp$ and B in the case of the spectrum in pyridine.

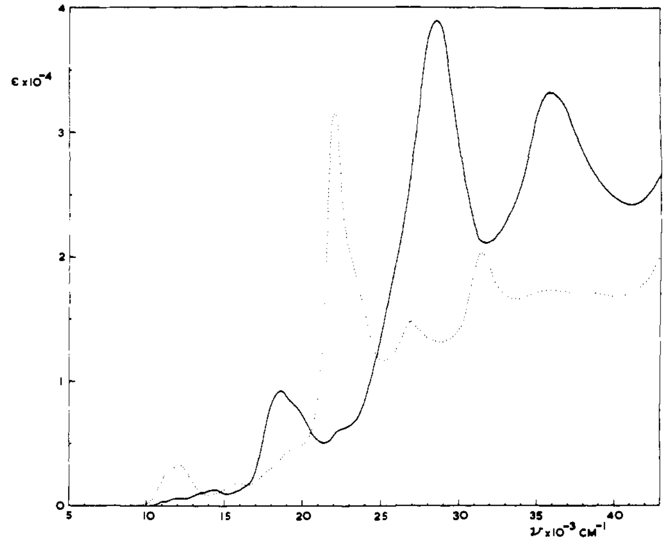

Figure 7. Electronic spectra of the first reduction products of the nickel(II) and cobalt(II) 1,19-diethoxycarbonyltetradehydrocorrins in THF: A (···), nickel complex; B (—), cobalt complex.

B. Reduced Species. Before discussing the reduced species of the nickel(II) and cobalt(II) 1,19-diethoxycarbonyltetradehydrocorrins, we may note that, on treatment with a methanolic solution of tetra-*n*-butylammonium hydroxide, both complexes undergo immediate hydrolysis and decarboxylation to give the corresponding 1-ethoxycarbonyltetradehydrocorrin (or more likely, the alkylammonium salt of the 1-carboxylic acid). The products were identified as 1-substituted tetradehydrocorrins by their electronic spectra, shown in Figure 6, which are very similar indeed to that of the nickel 1-methyltetradehydrocorrin.[23] Further confirmation of the nature of the products has been given by Grigg, *et al.*,[24] who have in fact isolated nickel 1-ethoxycarbonyl derivatives by a similar method.

We turn now to the reduced products of the 1,19-diethoxycarbonyltetradehydrocorrins. The first reduction product of the nickel complex generated by sodium film reduction in THF is shown in Figure 7A. Comparison of this spectrum with that in Figure 6A shows that the species is not simply a 1-substituted tetradehydrocorrin. The species also shows a strong radical esr signal at room temperature ($g = 2.0020 \pm 0.0002$; peak to peak width, 14.2 G).

The species is clearly, therefore, a radical, and reduction of the nickel(II) 2,12-diethyl-1,3,6,8,13,17,18-heptamethyltetradehydrocorrin (a related 1-substituted tetradehydrocorrin) shows that it is not a radical of a 1-substituted tetradehydrocorrin.[25] Exposing the solution to air produces *no* change in either the optical or esr spectrum of the radical for more than 1 hr, and the species is only slowly oxidized back to the parent complex over

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[23] D. A. Clarke, *et al.*, *J. Chem. Soc. C*, 1648 (1967).
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[25] I. S. Woolsey, Ph.D. Thesis, University of Bristol, 1970.

a period of several hours. The radical is, therefore, remarkably air stable. However, the parent complex may be quantitatively regenerated by treatment of the reduced species with oxidizing agents such as $FeCl_3$ or I_2.

The stability of the radical formed is reflected in the first reduction potential of the parent cation in DMF, which is −0.30 V, and corresponds to a one-electron reduction. On this basis, therefore, the reduced species is considered to be the neutral radical obtained by a simple one-electron addition to the lowest vacant ligand π orbital of the parent complex, *i.e.*

$$[Ni^{II}\text{-}1,19\text{-}(CO_2Et)_2Cn]^+ \xrightarrow{e} [Ni^{II}\text{-}1,19\text{-}(CO_2Et)_2Cn]\cdot$$

where Cn represents the tetradehydrocorrin ring (Table II).

Table II. Reduction Potentials of $[Ni^{II}\text{-}1,19\text{-}(CO_2Et)_2Cn]^+NO_3^-$ and $[Co^{II}\text{-}1,19\text{-}(CO_2Et)_2Cn]^+ClO_4^-$ in DMF[a]

Complex	Reduction potential (V *vs.* sce) 1st	2nd	3rd
$[Ni^{II}\text{-}1,19\text{-}(CO_2Et)_2Cn]^+NO_3^-$	−0.30	−1.71	−2.20
$[Co^{II}\text{-}1,19\text{-}(CO_2Et)_2Cn]^+ClO_4^-$	−0.16	−1.51	−2.16

[a] Using 0.1 *M* tetra-*n*-propylammonium perchlorate supporting electrolyte, with sample concentrations of 5×10^{-4} *M*. All reductions are one-electron processes.

Very recently, Hamilton and Johnson reported the isolation of two free radicals obtained by treatment of nickel(II) 8,12-diethyl-1,2,3,7,13,17,18,19-octamethyltetradehydrocorrin nitrate, $[Ni^{II}\text{-}1,19\text{-}Me_2Cn]^+NO_3^-$, with methanolic KCN.[26] Although complete characterization of the radicals was not given, it seems highly likely that they are the 5-cyano and 5,15-dicyano radical derivatives of the nickel(II) 8,12-diethyl-1,2,3,7,-13,17,18,19-octamethyltetradehydrocorrin, analogous to the 1,19-diethoxycarbonyl species described here.

Reduction of the cobalt(II) complex generates the species whose electronic spectrum is shown in Figure 7B. The spectrum is entirely different from that observed for the first reduction product of the nickel complex but is, in fact, very similar to that of the parent nickel complex shown in Figure 2, more so than that of the parent cobalt(II) complex. The species shows no esr signal at room temperature or 77°K. As with the first reduction product of the nickel(II) complex, the cobalt species is stable in air over a period of several hours but may also be quantitatively oxidized back to the parent cobalt(II) complex by treatment with $FeCl_3$ or I_2 solution. The polarographic studies in DMF again show the first reduction to be a one-electron process, the reduction potential being −0.16 V. It seems almost certain therefore that this species is the neutral cobalt(I) complex, $[Co^{I}\text{-}1,19\text{-}(CO_2Et)_2Cn]$, formed by a simple one-electron reduction of the central cobalt ion. Cobalt(II) porphyrins,[5c,11] phthalocyanines,[6,7] and vitamin B_{12r}[2,11,27] all give cobalt(I) species on reduction, but the cobalt(I) 1,19-disubstituted tetradehydrocorrin species described here is much more stable to reoxidation than the others.

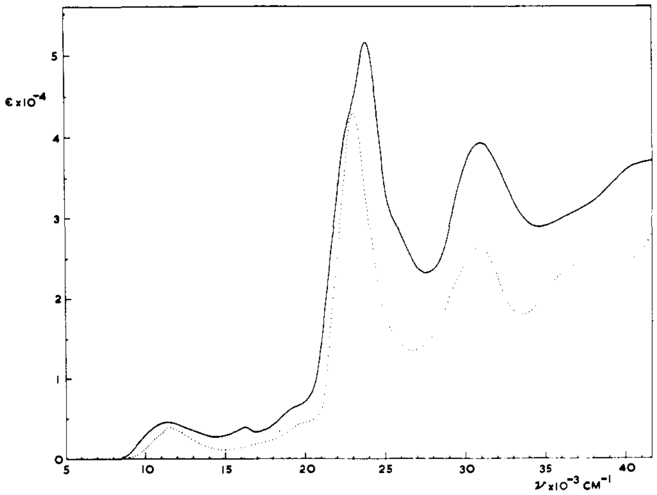

Figure 8. Electronic spectra of the second reduction products of the nickel(II) and cobalt(II) 1,19-diethoxycarbonyltetradehydrocorrins in THF: A (· · ·), nickel complex; B (—), cobalt complex.

The weak bands in the electronic spectrum of the cobalt(I) species are probably metal to ligand charge-transfer bands, so that the spectrum corresponds very closely indeed with that observed for $[Ni^{II}\text{-}1,19\text{-}(CO_2Et)_2Cn]^+$. This is as might be expected when one considers that the central metal ions in the two cases are likely to be almost isoelectronic.

Further reduction of the $[Ni^{II}\text{-}1,19\text{-}(CO_2Et)_2Cn]$ radical gives a diamagnetic species, whose electronic spectrum is shown in Figure 8A. Aerial oxidation of this species immediately regenerates more than 80% of the previous reduction stage (*i.e.*, the stable radical). Again studies of the reduction of nickel(II) 2,12-diethyl-1,3,7,8,13,17,18-heptamethyltetradehydrocorrin indicate that the species is not a reduction product of a 1-substituted tetradehydrocorrin.[25] The polarographic studies show that a second one-electron reduction of the parent complex occurs at −1.71 V in DMF, and we therefore assign the second reduction product of the nickel complex as the species $[Ni^{II}\text{-}1,19\text{-}(CO_2Et)_2Cn]^-$, with two extra electrons located in the ligand π orbitals.

Further reduction of the $[Co^{I}\text{-}1,19\text{-}(CO_2Et)_2Cn]$ complex generates the species whose electronic spectrum is shown in Figure 8B. The spectrum of this species is very similar indeed to that observed for the second reduction product of the nickel complex. Since the electronic spectra of these species are determined very largely by the nature of the ligand π MO's, this suggests that the second reduction products of the nickel and cobalt complexes have the same ligand structure and the same number of ligand π electrons. The second reduction product of the cobalt complex also shows a fairly strong cobalt resonance in the esr spectrum in frozen solution. A weak single line radical resonance is also observed during the reduction to form this species ($g = 2.0041 \pm 0.0004$; peak to peak width, 13.3 ± 0.5 G), but its low intensity suggests that this arises from either impurities in the sample or traces of breakdown products in solution and not to the bulk of the cobalt species present in solution. This is further supported by the fact that this resonance disappears while the cobalt resonance remains when reduction to the second stage is complete. No cobalt esr signal was observed at room temperature. The cobalt resonance varies somewhat with the exact point in the re-

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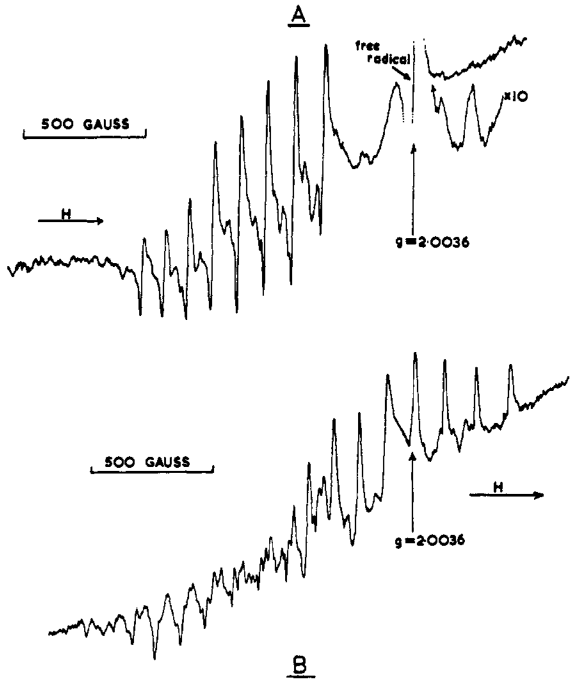

Figure 9. Esr spectra of the second reduction product of cobalt(II) 1,19-diethoxycarbonyltetradehydrocorrin in THF solution af 77°K. Spectra A and B correspond to the species whose electronic spectrum is shown in Figure 8B, but spectrum B is observed on slight further reduction of spectrum A.

duction at which it is observed. The esr spectrum of a 10^{-3} M solution of the second reduction product of the cobalt complex in THF at 77°K shown in Figure 9B develops from that shown in Figure 9A when the solution is allowed to come into brief further contact with the sodium film. However, the electronic spectrum of the solution was not detectably changed by this process. This seems to indicate that the conjugated π system of the ligand is unaffected, and hence we believe the esr spectra to arise from essentially the same species. Similar effects have been observed during the reduction of chromium and nickel phthalocyanines under the same experimental conditions as those employed here,[9] but it is difficult to explain their origin. In the present case it is possible that the ethoxycarbonyl groups undergo some modification between the two situations represented by Figures 9A and B, for example, by being converted to the sodium salts of the corresponding carboxylic acid derivative. The electronic spectrum of this species would be virtually identical with that of the ethoxycarbonyl species, since the conjugated π system of the ligand is not changed. However, its esr spectrum might differ from that of the ethoxycarbonyl complex due to changes in solvation associated with the higher ionic charge of this species; the esr spectra of cobalt complexes of this type are known to be extremely sensitive to their environment.[16,17]

Aerial oxidation of the second reduction product of the cobalt complex immediately regenerates more than 90% of a species having an electronic spectrum the same as the previous reduction stage, and which showed no esr signal. In view of the preceding discussion, this could be either the [Co^{I}-1,19-$(\text{CO}_2\text{Et})_2$Cn] complex itself or the sodium salt of the corresponding carboxylic acid, since the acid salt would again be expected to have an electronic spectrum almost identical with that of the [Co^{I}-1,19-$(\text{CO}_2\text{Et})_2$Cn] complex. Whether the ethoxycarbonyl groups are modified in this way or not is of minor importance, however, the major consideration being that the species concerned are still cobalt complexes of the 1,19-disubstituted tetradehydrocorrin ligand. In the subsequent discussion therefore we have assumed that no modification of these groups has occurred and concern ourselves only with the nature of the reduction process involved.

The polarographic studies in DMF show the second reduction of the parent cobalt(II) complex to be a one-electron process, the reduction potential being -1.51 V. We therefore assign the second reduction product of the cobalt(II) 1,19-disubstituted tetradehydrocorrin observed in THF as a simple one-electron reduction product of the cobalt(I) species.

The problem arises in this case, however, as to the details of the electronic structure of the reduced species present. Three possibilities exist: either it is the cobalt(0) complex [Co^0-1,19-$(\text{CO}_2\text{Et})_2\text{Cn}]^-$, where the additional electron has again entered a molecular orbital primarily associated with the cobalt, or it is the cobalt(I) species [Co^{I}-1,19-$(\text{CO}_2\text{Et})_2\text{Cn}]^-$ with the extra electron located in the ligand π orbitals, or it could be the cobalt(II) species (Co^{II}-1,19-$(\text{CO}_2\text{Et})_2\text{Cn}]^-$ with the lowest vacant ligand π orbital of the parent complex now fully occupied. Of these possibilities, we may rule out the second on the basis that we would not expect the cobalt esr signal observed, but a strong radical esr resonance from the unpaired electron in the ligand π orbitals. We have already pointed out the very close similarity between the electronic spectra of the second reduction products of the nickel and cobalt complexes and noted that this suggests very strongly that the two have the same ligand π-electron structure. Since the second reduction product of the nickel complex has been shown to be [Ni^{II}-1,19-$(\text{CO}_2\text{Et})_2\text{Cn}]^-$, *i.e.*, a nickel(II) complex with the two extra electrons located in the ligand π orbitals, the optical spectrum of the second reduction product of the cobalt complex strongly suggests that the species is the cobalt(II) complex [Co^{II}-1,19-$(\text{CO}_2\text{Et})_2\text{Cn}]^-$, also with the two extra electrons located in the ligand π orbitals.

We have also noted in the case of the [Co^{I}-1,19-$(\text{CO}_2\text{Et})_2$Cn] complex that changes in oxidation state of the central metal ion do not produce very great modification of the electronic spectrum of the ligand. Thus we would expect the cobalt(0) complex, [Co^0-1,19-$(\text{CO}_2\text{Et})_2\text{Cn}]^-$, to exhibit an electronic spectrum similar to that observed for the [Co^{I}-1,19-$(\text{CO}_2\text{Et})_2$Cn] complex, since there is no change in the number of electrons formally associated with the ligand. This is not the case, however, and it may be concluded that the electronic spectrum of the second reduction product of the cobalt complex is only consistent with its formulation as the species [Co^{II}-1,19-$(\text{CO}_2\text{Et})_2\text{Cn}]^-$. Analysis of the cobalt esr spectrum exhibited by this species offers confirmation of its identity as a cobalt(II) complex rather than a cobalt(0) one.

The spectra were again analyzed by the methods of Kneubuhl and Walker in terms of the spin Hamiltonian given in eq 1. The g and hyperfine tensor components are given in Table I. It is worth pointing out that despite the rather different appearance of the two spectra, the parameters determined for the spin Hamiltonian are quite similar. This is consistent therefore with only minor differences between the species responsible for the two spectra. They are also similar to those observed for the parent cobalt(II) complex in THF. The low-field ($g_\perp$) lines of the spectrum in Figure 9B are considerably more complex than those in 9A. This complexity may arise from either of the effects mentioned previously in connection with the cobalt(II) resonance of the parent complex. It is also possible that it arises from solute crystallization effects giving rise to species with different local environments and a nonrandom orientation of the paramagnetic species in the matrix.[28] We do not believe therefore that the complexity of this part of the spectrum arises from superhyperfine coupling to the pyrrole nitrogens. Certainly, however, the high-field lines ($g_\parallel$) do not show any observable coupling. The values quoted for $g_\perp$ and B for spectrum 9B correspond as before to the strongest series of cobalt hyperfines observed. The value given for $g_\parallel$ for Figure 9A is difficult to determine accurately due to the weakness of the hyperfine lines and the presence of the radical resonance mentioned previously.

If the species responsible for the observed cobalt resonances were cobalt(0) complexes, the central cobalt atom would possess nine 3d electrons and be isoelectronic with the Cu^{2+} ion. Since we have a nearly square-planar ligand environment, the species should then be analogous to copper(II) complexes of porphyrins and phthalocyanines. Here the unpaired electron is found to reside in the in-plane $d_{x^2-y^2}$ orbital of the copper ion[7,16,29,30] and in this situation $g_\parallel$ is observed to be greater than $g_\perp$.[7,16,29,30] These complexes also exhibit a nine-line superhyperfine coupling due to the four coordinating pyrrole nitrogens of about 15 G on both g-tensor components.[16,29,30] We do not observe such superhyperfine coupling, however, and in our spectra $g_\perp > g_\parallel$. The esr spectra are not consistent therefore with the formulation of the species as a cobalt(0) complex.[31] They are, however, compatible with their formulation as cobalt(II) species, in which case the unpaired electron would be located in either the d_{z^2} or d_{xy} orbital of the cobalt ion.[32a] In both these cases $g_\parallel < g_\perp$,[32] and a large hyperfine coupling to the pyrrole nitrogens is not expected.

Both the cobalt and nickel 1,19-diethoxycarbonyltetradehydrocorrins may be reduced beyond the second reduction stage, but the products are no longer as well defined and do not regenerate the earlier reduction products on aerial oxidation. Consequently we limit further discussion to the reduction products previously described.

Conclusions and Comparisons with Vitamin B_{12}

It is readily appreciated that the reduced products of the nickel and cobalt 1,19-disubstituted tetradehydrocorrins are rather exceptional. The first reduced species is a remarkably stable neutral radical in the case of the nickel complex and an equally stable cobalt(I) species in the case of the cobalt complex, while the second reduction products are both metal(II) complexes with two extra electrons in the ligand π orbitals. It is interesting to note that in the original synthesis of the 1,19-dimethyl-substituted complexes,[4] the second reduction product observed in this study was postulated as an intermediate in the synthesis of the parent complexes, the parent complex being obtained by continued aerial oxidation of the intermediate. This lends further support to our assignments of the second reduction products as metal(II) complexes, since the intermediate (*i.e.*, the second reduction product described here) was synthesized from the metal(II) acetate and 1,19-dideoxy-8,12-diethyl-1,2,3,7,13,17,18,19-octamethylbiladiene-*ac* dihydrobromide. In addition, it indicates that cyclization precedes oxidation in the formation of the metal(II) 1,19-disubstituted tetradehydrocorrins from the linear tetrapyrrole starting material, a point not yet established in the synthesis of these complexes.[33] It is also most unlikely that a cobalt(0) species would be formed under the conditions used for cyclization of the biladiene complex with cobalt(II) acetate.[4]

The cobalt species represent a remarkable series in which the oxidation state of the central cobalt ion changes from II $\rightarrow$ I $\rightarrow$ II with successive electron addition. The final change from cobalt(I) to cobalt(II) must result from tranfer of an electron on the cobalt(I) ion to the ligand, together with concurrent ligand reduction. Apparently it is more favorable to have the electrons spin paired in the ligand π orbitals than to have one on the central cobalt(I) ion and one in the ligand orbitals. To our knowledge the present study is the first in which such an oxidation sequence has been established.

Although the first reduction product of the cobalt(II) 1,19-diethoxycarbonyltetradehydrocorrin is a neutral cobalt(I) complex, the lowest vacant ligand π orbital of the parent cobalt(II) complex must be very low in energy, as indicated by the very low first reduction potential of the nickel(II) complex where ligand reduction occurs (-0.30 V compared with -0.16 V for the cobalt(II) complex). It might therefore be possible to effect internal electron transfer from the the cobalt(I) ion to the ligand under different experimental conditions to give a cobalt(II) species with the additional electron in the ligand π orbitals. The presence of such low-lying vacant orbitals could play an important part in the chemistry of the complex, and it is interesting, therefore, to consider whether such effects may be possible in the redox properties of cobalt corrins. Figure 10 shows a plot of the SCF energy of the lowest vacant π orbital of various conjugated tetrapyrrole ligands against the first reduction

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(28) H. Fierz and A. von Zelewsky, *Inorg. Chem.*, 10, 1556 (1971). This effect is also a further possibility in the case of the parent cobalt(II) complex (Figure 4) and is made likely by the rather low solubilities of the complexes in THF.

(29) E. M. Roberts and W. S. Koski, *J. Amer. Chem. Soc.*, 83, 1865 (1961).

(30) E. M. Roberts and W. S. Koski, *ibid.*, 82, 3006 (1960).

(31) Rollman and Iwamoto have postulated that the second reduction product of cobalt(II) tetrasulfonated phthalocyanine is a cobalt(0) species on the basis that the esr signal observed shows $g_\parallel > g_\perp$, but this has recently been questioned by Walker,[17] who indicates that the species may well be a superoxo complex of cobalt(II) produced by decomposition of the DMSO solvent. Experiments in the author's laboratory on the unsulfonated cobalt(II) phthalocyanine also indicate that the second reduction product is not a cobalt(0) one,[8] as do those of Taube.[6]

(32) (a) J. S. Griffith, *Discuss. Faraday Soc.*, 26, 81 (1958); (b) A. H. Maki, N. Edelstein, A. Davidson, and R. H. Holm, *J. Amer. Chem. Soc.*, 86, 4580 (1964).

(33) I. D. Dicker, *et al.*, *J. Chem. Soc. C*, 536 (1971).

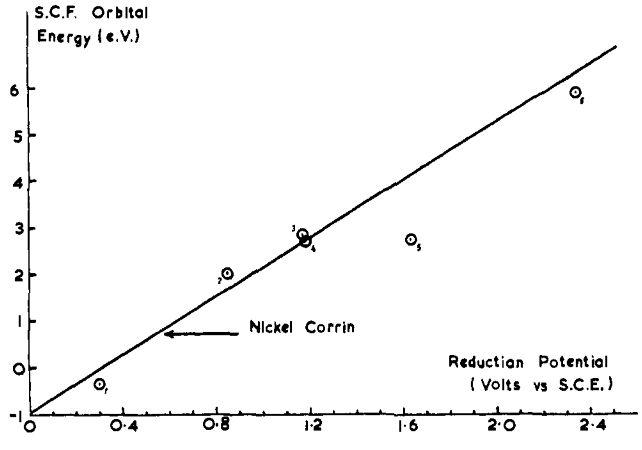

Figure 10. Plot of SCF energy of the lowest vacant ligand π orbital against the first reduction potential of the nickel(II) complex of various tetrapyrrole ligands. (See Table III for numerical data.)

potential of their nickel(II) complex (see also Table III).[34] The SCF orbital energy of the lowest vacant π orbital of the corrin ligand, which has a_2 symmetry, assuming C_{2v} symmetry for the ligand, has been found to be 0.718 eV, which would indicate a reduction potential of about -0.55 V for a nickel(II) corrin in an aprotic solvent such as DMF. Nickel(II) corrins are known,[36,37] but to the authors' knowledge, the reduction potentials of these species have not been measured. It would be most illuminating if this were done, since a value of -0.55 V is rather positive, more positive than the reduction potentials of the nickel phthalocyanine or porphyrin complexes.

Table III. First Reduction Potentials and Calculated Energies of Lowest Vacant Ligand π Orbital for Nickel(II) Complexes of Various Tetrapyrrole Ligands

	Complex[a]	First reduction potential[b]	Lowest vacant ligand π-orbital energy[c]	Ref
1.	$[\mathrm{Ni^{II}\text{-}1,19\text{-}(CO_2Et)_2Cn}]^+\mathrm{NO_3}^-$	-0.30	-0.337	12
2.	$\mathrm{Ni^{II}Pc}$	-0.85	2.007	38
3.	$\mathrm{Ni^{II}}$-1-MeCn	-1.17	2.854	12
4.	$\mathrm{Ni^{II}TPP}$	-1.18	2.712	5
5.	$\mathrm{Ni^{II}}$-20-EtCn	-1.63	2.757	12
6.	$\mathrm{Ni^{II}C^-}$	-2.34	5.919	12

[a] Complexes 3 and 5 are 1-methyl- and 20-ethyl-substituted nickel tetradehydrocorrins, while complex 6 is the nickel(II) corrole anion. [b] *vs.* sce in DMF except for 4, which is for a DMSO solution. [c] Calculated using the SCF variable bond order method of Nishimoto and Forster.[35] The orbital energies quoted are in electron volts and that for the corrin ligand is 0.718 eV.

Turning now to the cobalt complexes of these tetrapyrrole ligands where cobalt(I) species are generated on reduction, the reduction potentials have been given as -0.37 V for cobalt(II) phthalocyanine in DMF,[38] -0.547 V for the tetrasulfonated derivative in DMSO,[7] and -0.82 V for cobalt(II) tetraphenylporphine in DMSO.[5c] Several studies have been made of the polarographic reduction of various vitamin B_{12} derivatives to form cobalt(I) species,[39–42] but all have been carried out in aqueous solution so that direct comparison with the results quoted above for measurements in aprotic solvents is not possible. However, Momenteau, *et al.*,[11] have shown that the ease of reduction of these species in *N*,*N*-dimethylacetamide is $\mathrm{Co^{II}}$ Pc > vitamin B_{12r} > $\mathrm{Co^{II}}$ TPP. It is reasonable therefore to assume a reduction potential for vitamin B_{12r} in aprotic solvents of this type of -0.6 to -0.7 V *vs.* sce. This is actually more negative than the predicted reduction potential of the nickel(II) corrin, where ligand reduction would occur. Although we know from experiment that reduction of vitamin B_{12r} generates a cobalt(I) species, it seems likely that there are relatively low-lying vacant ligand orbitals which might well influence its chemical activity. Since the cobalt(I) species is thought to play an important role in the biochemical activity of vitamin B_{12},[2] it would be very interesting to test this suggestion.

In conclusion we may add that further study of the physicochemical properties of metal derivatives of these 1,19-disubstituted tetradehydrocorrins and their reduced species would be extremely interesting in view of their unique behavior and structural similarity to the vitamin B_{12r} species, and they could be usefully employed as model systems for comparison with the B_{12} complexes. Furthermore, the present work suggests that the presence of the ligand π orbitals should be taken into consideration when dealing with reduced species of vitamin B_{12} derivatives.

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(34) The π-orbital energies for the complex were calculated using the variable bond order π-SCF-MO method of Nishimoto and Forster.[35] The parameterization of the method was also that used by Nishimoto and Forster. The first reduction products of all these complexes are species in which one-electron reduction of the ligand π system occurs.

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