Table I. Major Band Centers in the Absorption (77 K) and MCD (2.8 K) Spectra of $[MgPc(-3)]^{\bullet-}$

	wavelength/nm (MCD sign)									
abs	360		428	569	643	790	855		923	952
MCD	380(+)	406(−)	428(−)	569(+)	[635](−)	785(−)	840(−)	880(+)	923(+)	952(−)

Table II. Splitting Energy between ± Pairs of Bands in the MCD (2.8 K) and Absorption (77 K) Spectra of $[MgPc(-3)]^{\bullet-}$

	range/nm	MCD band pair/nm	energy diff/cm^{-1}
set i	300–450	380–428	2950
set ii	500–700	569–643	2050
set iii	850–1000	923–952	330

The absorption and MCD spectra shown in Figure 1C–F are quite unusual when compared with spectra of other metallophthalocyanines.[19a] The absence of derivative-shaped *A* terms contrasts with the strong *A* terms which dominate the spectra of MgPc(−2) (Figure 1B) and the π-cation-radical $[MgPc(-1)]^{\bullet+}$ species.[16,17] The band centers are summarized in Table I. It should be noted that the shoulder near 670 nm in the absorption spectrum and the weak positive *A* term in the MCD spectrum are due to minor fractions of the extremely intense Q band ($\epsilon \sim 200\,000$) of MgPc(−2). The spectrum of the anion radical is therefore composed entirely of *B* terms. We note that this means that, with a nondegenerate ground state, each excited state is also nondegenerate (Figure 2). A recurring spectral feature centered on 950, 640, and 430 nm can be seen that involves pairs of oppositely signed *B* terms. The overall features can therefore tentatively be identified as three series of transitions (based on a ± sequence in the MCD spectrum) that make up the bands seen between (i) 300 and 450 nm, (ii) 500 and 700 nm, and (iii) 850 and 1000 nm.

The $\pi-\pi^*$ transitions of metallophthalocyanines are usually explained in terms of a 16-membered cyclic polyene containing 18 electrons.[13,26] The electronic structure of an ideal cyclic polyene would contain orbitals with 0, ±1, ±2, ..., ±7, 8 orbital angular momentum units. The four-electron LCAO model of Gouterman has been successful in predicting the spectra that arise when the ring is distorted by the addition of aza linkages of the phthalocyanine dianion ligand, which is predicted to lift the degeneracy of each ungerade, degenerate orbital.

The lifting of the orbital degeneracy of e_g^* is probably caused by a Jahn–Teller splitting of the anticipated ^2E_g ground state. Minor et al.[34] used a similar argument to explain the lack of EPR signal for $[MgPc(-4)]^{2-}$, a species which would be expected to have a $^3A_{2g}$ ground state. Transitions into closely linked Jahn–Teller-split states can be expected to give rise to coupled pairs of oppositely signed *B* terms similar to those which dominate the MCD spectrum.[26] For pairs of states, which are relatively isolated, the resulting MCD *B* terms will be *x* and *y* polarized and will sum to zero.[25,26] The separation of these bands will be determined by the splitting of the orbitals.

The splitting between each ± pair in the MCD spectrum is different, ranging from 330 to 2950 cm^{-1} (Table II). We tentatively associate bands between 300 and 450 nm (388/428 nm) and between 850 and 1000 nm (923/952 nm) as belonging to a set characterized by narrow, unsplit bands, followed by lower intensity bands. The band system at 569/635 nm, which is characterized by two pairs of oppositely signed *B* terms, appears to belong to a second set. We suggest that the bands in the first set arise from $\pi-\pi^*$ transitions into the Jahn–Teller-split e_g^* orbital, which represent the original Q and B_1/B_2 bands. The 923/952-nm splitting of 330 cm^{-1} then may represent Jahn–Teller splitting of the e_g^* orbital. We think that the band system in the 300–450-nm region is more complex and comprises both $\pi-\pi^*$ (the B_1 and B_2 bands) and $\pi^*-\pi^*$ bands. The 569/643-nm bands probably arise from transitions out of the split e_g^* into the b_{1u}^* and b_{2u}^* orbitals (see Figure 1). The 2050-cm^{-1} split would therefore represent the energy difference between b_{1u}^* and b_{2u}^*. Our rationale for these choices of orbitals is as follows. (i) The 923/952-nm bands and the 388/428-nm bands exhibit very narrow bandwidths, with apparent vibrational bands lying to higher energy, much like the Q band shown for MgPc in Figure 1A. (ii) We associate the larger extinction coefficients at 569 and 643 nm with transitions out of the e_g^* orbital into b_{1u}^* and b_{2u}^* orbitals that are reportedly significantly split in neutral complexes.[13] (iii) We assume a general red shift of the MPc(−2) spectrum of about 4500 cm^{-1} is associated with ring reduction.

In summary, room- and low-temperature MCD spectroscopies have provided valuable information unavailable from absorption spectra alone. These data provide unambiguous evidence that the ground and excited states of $[MgPc(-3)]^-$ are nondegenerate.

Acknowledgment. We wish to acknowledge funding from the NSERC of Canada through operating and equipment grants. We thank Joe Oceapia for his advice on the design of the spectroelectrochemical cells. We are associated with the Centre for Chemical Physics and the Photochemical Unit at the UWO. This is publication number 450 of the Photochemical Unit.

Registry No. $[MgPc(-3)]^{\bullet-}$, 32458-93-8.

(34) Minor, A. P.; Gouterman, M.; Lever, A. B. P. *Inorg. Chem.* **1985**, *24*, 1894.

Contribution from the Department of Chemistry, Emory University, Atlanta, Georgia 30322

Treatment of Vitamin B_{12} and Aquocobalamin (B_{12a}) with the Efficient Hydrolytic Agent $[Co(trpn)(H_2O)_2]^{3+}$

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Introduction

Considerable effort has been expended recently on promoting the hydrolysis of phosphate esters because of the utility of phosphodiester hydrolysis reactions in probing DNA and RNA sequences and structure.[1] However, another phosphodiester group of biochemical interest exists in B_{12} compounds. Here, the phosphodiester group forms part of the linkage between the axial 5,6-dimethylbenzimidazole group and the equatorial corrin ring (Chart I, which also gives the IUPAC atom numbering scheme). Cleavage of this group requires rather drastic conditions, but the resulting cobinamides are very useful for understanding the role of steric effects on the B_{12} cofactor during the Co–C bond homolysis step in enzymic processes.[2] A milder cleaving agent would thus be very useful for the preparation of cobinamides.

One of the most effective agents promoting phosphodiester hydrolysis is the complex $[Co(trpn)(H_2O)_2]^{3+}$ (trpn = tris-(3-aminopropyl)amine) studied primarily by Chin and co-workers.[3-6] Therefore, we have probed the potential utility of this promising

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(2) Hay, B. P.; Finke, R. G. *J. Am. Chem. Soc.* **1987**, *109*, 8012–8018.
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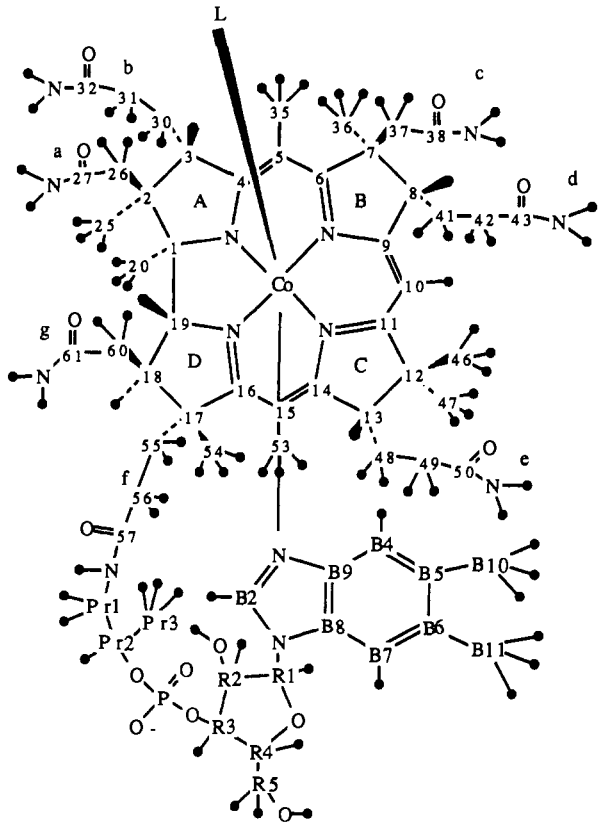
0020-1669/92/1331-1719$03.00/0

Chart I. L = CN^- (Vitamin B_{12}, CNB_{12}); H_2O (B_{12a})



agent on the hydrolysis of the phosphodiester bonds in cyanocobalamin (vitamin B_{12}, CNB_{12}) and aquocobalamin (B_{12a}). The study should serve to assess the applicability of this complex with true biological substrates.

The Co(III) amine complexes are particularly valuable for such studies since the Co(III) center produces well-defined complexes with phosphate ligands. These complexes are easily identified using ^{31}P NMR spectroscopy.[4,5,7]

Experimental Section

$[Co(trpn)(H_2O)_2](ClO_4)_3$ was synthesized according to reported procedures.[8] Anal. Calcd for $C_9H_{28}Cl_3CoN_4O_{14}$: C, 18.59; H, 4.85; N, 9.63. Found: C, 18.74; H, 4.80; N, 9.47. "Hydroxocobalamin acetate" from Roussel and cyanocobalamin from Sigma were used without further purification.

pH-meter readings were obtained directly from the NMR sample in either 5-mm or 10-mm NMR tubes with a 0.3 mm × 20 cm pH electrode (Ingold). In D_2O, the value was corrected by using the relationship pD = pH + 0.4.[9] The pD was adjusted with NaOD and $DClO_4$.

Reactions were carried out in D_2O (pD 5) at room temperature, 35 and 45 °C at 4:1 and 12:1 ratios of $[Co(trpn)(H_2O)_2]^{3+}$ to cobalamin (5 mM). In addition, the reaction was carried out at 35 °C at a 1:1 molar ratio, as well as at 5 °C at a 12:1 ratio. Furthermore, reactions at pD 7 were carried out at room temperature and 45 °C at a 4:1 ratio of $[Co(trpn)(H_2O)_2]^{3+}$ to CNB_{12} or B_{12a} (5 mM), as well as at a 12:1 ratio of $[Co(trpn)(H_2O)_2]^{3+}$ to B_{12a} (5 mM). As reported previously, buffers could not be used since they cause dimerization of the cobalt complex.[4] The pD was kept at ~7 by successive additions of $DClO_4$. When no acid was added during the reaction, the pD increased to a final value of ~8.7. The progress of the reactions with time was followed with ^1H and ^{31}P NMR spectroscopy. The NMR tubes were kept wrapped with aluminum foil to minimize exposure to light.

^1H NMR spectroscopy was performed using Nicolet 360-MHz and General Electric QE-300 spectrometers. Spectra were recorded on samples dissolved in 99.9% D_2O in 5-mm tubes with the following parameters: 25° pulse; presaturation of HOD; 16K data points; 0.1-Hz line broadening; 16–64 scans. Reported chemical shifts were based on NaTSP (sodium 3-(trimethylsilyl)tetradeuteriopropionate) as internal reference.

^{31}P NMR spectra of the same samples, usually in 5-mm tubes, were recorded at 81.01 MHz with an IBM WP-200SY spectrometer and typically used TMP (trimethyl phosphate) in D_2O as an external reference. Typical instrumental conditions were as follows: 5-Hz line broadening; 4K data points; 3-s relaxation delay; 46° pulse; spectral width 3000 or 4000 Hz; broad-band proton decoupling; 3000–16000 scans.

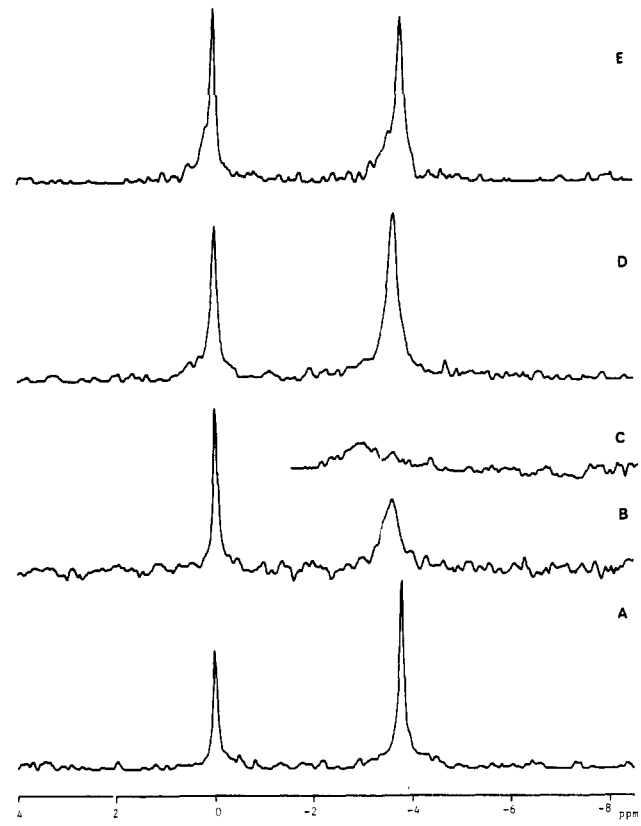


Figure 1. ^{31}P NMR spectra in D_2O: (A) CNB_{12}, 5 mM, pD 6.9; (B) solution of $[Co(trpn)(H_2O)_2]^{3+}$ and CNB_{12} (4:1), pD 6.9, after 1 h at room temperature; (C) solution of $[Co(trpn)(H_2O)_2]^{3+}$ and CNB_{12} (4:1), pD 7, after 1 day at room temperature; (D) solution of $[Co(trpn)(H_2O)_2]^{3+}$ and CNB_{12} (4:1), pD 6.8, after 5 days at room temperature, with ca. 20 mM EDTA and TMP as an external reference; (E) solution of $[Co(trpn)(H_2O)_2]^{3+}$ and CNB_{12} (4:1), pD 7, after 5 days at room temperature, with EDTA (20 mM) and TMP as an internal standard.

Results and Discussion

As discussed in depth below, all the ^1H and ^{31}P NMR studies are consistent with the decomposition of $[Co(trpn)(H_2O)_2]^{3+}$ under all conditions studied and with the absence of hydrolysis of either CNB_{12} or B_{12a}. However, the ^1H NMR results indicate the formation of one initial major new cobalamin product (I) with B_{12a}. After extended time periods, a second product (II) is formed in comparable amounts. Neither I nor II are formed by CNB_{12}.

In this study, the ratio of $[Co(trpn)(H_2O)_2]^{3+}$ to substrate was lower than those used previously,[3-6] because our goal was to develop a preparative method. We utilized $[Co(trpn)(H_2O)_2]^{3+}$ concentrations within the range used previously.[4] Under these conditions, we were concerned about dimerization.[4,8] Furthermore, the $[Co(trpn)(H_2O)_2]^{3+}$ is readily converted by adventitious CO_2 to the stable carbonato complex at higher pH. Although the optimal pH for the hydrolysis of phosphodiesters by $[Co(trpn)(H_2O)_2]^{3+}$ is ~6.2, we initially selected pD 5 in order to minimize dimerization.[8] The hydrolysis rate is expected to be only ~33% slower at pD ~5 than at pD ~6.2.[8] However, a reviewer suggested we evaluate the hydrolysis at higher pD where decomposition may not be important. We selected pD 7 because the rate of hydrolysis should approximate that at pD 5.[8]

^{31}P NMR Spectroscopy. The ^{31}P NMR signal of CNB_{12} at pD 6.9 appears at −3.8 ppm relative to external TMP (Figure 1).

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Table I. Selected ^1H NMR Results for B_{12a} and Products Formed with trpn at pD 5[a]

assignment	B_{12a}	I	II
B7H	7.16	7.20	7.21
B2H	6.51	6.78	6.81
B4H	6.44	6.35	6.40
C10H	6.29	6.29	6.29
R1H	6.23	6.13	6.04
$C36H_3$	1.94		
$C25H_3$	1.51		
$C47H_3$	1.49		
$C54H_3$	1.39		
$C46H_3$	1.36		
$Pr3H_3$	1.26[b]	1.26	1.26
$C20H_3$	0.51	0.37	0.40

[a] Shifts relative to internal TSP. [b] Doublet.

Upon addition of the $[Co(trpn)(H_2O)_2]^{3+}$, after 1 h, the signal broadens and shifts slightly downfield to ~−3.6 ppm. However, no changes are observed in the ^1H NMR spectrum. If a solution of $[Co(trpn)(H_2O)_2]^{3+}$ and CNB_{12} (4:1) is kept at room temperature for 1 day, a very broad ^{31}P NMR signal is observed. After 5 days at room temperature and addition of EDTA, the signal sharpens and appears at −3.6 ppm relative to *external* TMP. However, if *internal* TMP is added to this solution and used as a reference, the signal appears at −3.8 ppm (Figure 1). These results suggest that the broadening as well as the downfield shift (relative to external TMP) of the CNB_{12} ^{31}P NMR signal are due to the presence of paramagnetic Co^{2+}.

To determine whether the products found with B_{12a} were the result of hydrolysis of the phosphate ester linkage, we monitored the ^{31}P NMR spectrum during the reaction. The ^{31}P NMR signal of B_{12a} in aqueous solution at pD 5 occurs at −3.7 ppm relative to external TMP. On addition of the $[Co(trpn)(H_2O)_2]^{3+}$, the signal broadens and shifts slightly downfield to −3.4 ppm. These initial changes are unlikely to be due to a B_{12a} reaction since there are no accompanying changes in the ^1H NMR spectrum. This initial broadening of the ^{31}P NMR signal depends to some extent on the ratio of $[Co(trpn)(H_2O)_2]^{3+}$ to B_{12a} and on the presence of EDTA. However, if a solution of $[Co(trpn)(H_2O)_2]^{3+}$ and B_{12a} (12:1) is kept at room temperature for 5 days, only a very broad ^{31}P NMR signal is observed at ~−3.4. Upon addition of EDTA, the signal sharpens, but appears at the same shift. No other signals were observed between 45 ppm and −15 ppm. Furthermore, even when solutions were kept longer, e.g., 73 days, only one signal was found.

If hydrolysis had occurred, we would have expected to see signals vs TMP at ca. +17 ppm due to coordination of the phosphate monoester to Co(III). Alternatively, further hydrolysis to the nucleoside and the phosphate complex should have produced a binuclear complex with a signal at +37 ppm.[4] Coordination to the phosphodiester group, the common metal binding site, would have given a downfield-shifted signal. No such signals were observed. We conclude that there are no coordinated phosphate groups.

The $[Co(trpn)(H_2O)_2]^{3+}$ was found to decompose, leading to the formation of the free protonated ligand trpn and Co^{2+}, as evidenced by an increase in pH (to pD ~8.7), sharp ^1H NMR signals at 3.3, 3.1, and 2.1 ppm for free protonated trpn after the pD was lowered to 5, and extensive ^{31}P NMR line broadening, even at pD 5. The presence of Co^{2+} would broaden and shift slightly downfield (vs external TMP) any ^{31}P NMR signals of uncoordinated phosphate monoester or phosphate ions. However, addition of EDTA greatly sharpened the ^{31}P NMR signals, and no signals not attributable to the B_{12a} were observed. On the basis of ^{31}P NMR spectroscopy on CNB_{12} and B_{12a}, it does not appear that $[Co(trpn)(H_2O)_2]^{3+}$ can either promote the hydrolysis of the phosphodiester bonds or coordinate to the phosphodiester group to any significant extent.

^1H NMR Spectroscopy. In all cases, ^1H NMR spectra of pD 5 solutions containing $[Co(trpn)(H_2O)_2]^{3+}$ and B_{12a} at time zero are very similar to the sum of the spectra of B_{12a} (Table I)[10] and

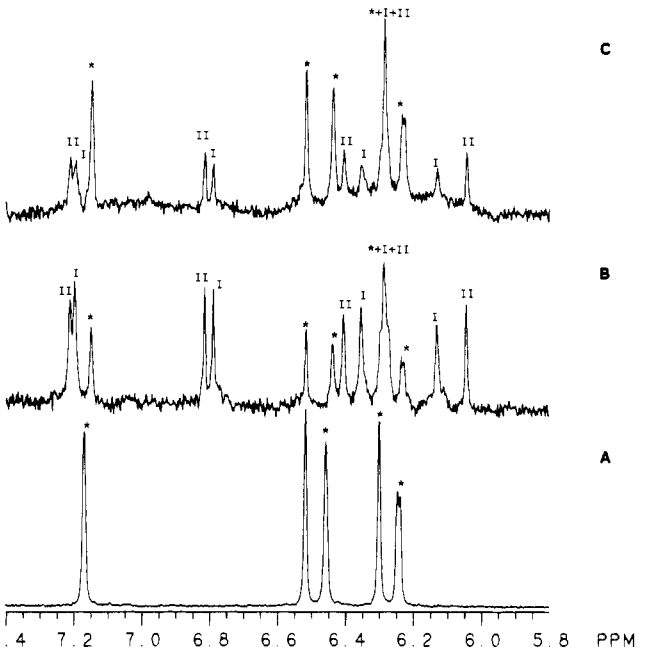

Figure 2. ^1H NMR spectra in D_2O of the aromatic region: (A) B_{12a}, 5 mM, pD 4.9 (designated with an asterisk); (B) solution of $[Co(trpn)(H_2O)_2]^{3+}$ and B_{12a} (12:1), pD 5, after 28 h at 35 °C and 22 h at 5 °C [note that new species are present (signals designated with I and II); also the B_{12a} signals are slightly shifted (<0.030 ppm) compared to pure D_2O solutions]; (C) solution of $[Co(trpn)(H_2O)_2]^{3+}$ and B_{12a} (12:1), pD 5, after 28 h at 35 °C and 6 days at 5 °C.

$[Co(trpn)(H_2O)_2]^{3+}$ and $[Co(trpn)(CO_3)]^+$ (3.06, 2.83*, 2.61*, 2.40, 2.24, 2.15, 2.03* and 1.85** ppm). Signals exclusively for the carbonato complex are indicated by two asterisks, and overlapping aquo and carbonato signals are indicated by a single asterisk.

In order to check the influence of temperature on the formation of the new species, different conditions were examined using solutions that were 12:1 or 4:1 in $[Co(trpn)(H_2O)_2]^{3+}$ and B_{12a}. For the 12:1 solutions at room temperature, 35, and 45 °C, signals for two major products, labeled I and II, indicated the reaction had progressed 20% after 24, 7, and 2.5 h, respectively. After 6 h, only signals of B_{12a} are observed at room temperature, whereas at 35 and 45 °C the reaction has proceeded by 20% and 67%, respectively. At 5 °C, no appreciable formation of I or II was observed, even after 7 days. These results suggest that the reaction was greatly favored at elevated temperature, probably due to the greater rate of decomposition of $[Co(trpn)(H_2O)_2]^{3+}$.

These changes in the ^1H NMR spectra can be due either to hydrolysis of some of the amide side chains[11] or to the formation of adducts between the B_{12a} and trpn. In order to characterize the new products, two regions of the ^1H NMR spectrum are useful, namely the aromatic region (Figure 2) and the upfield methyl region (Figure 3). The signals in these regions that can easily be assigned to each product are given in Table I. Assignments to a given type of proton are tentative and are based on the proximity of previously assigned aquocobalamin signals.[10] It is immediately clear that the two products must be closely related since the shifts are very similar. We can rule out amide hydrolysis since the products can be converted back to B_{12a} by acidification of the solutions, as discovered initially by adding EDTA and adjustment of the pD. The B_{12a} is more favored at the lower temperature, 5 °C (Figure 2).

Although the pD was adjusted periodically to ~5, it is possible that the protonated trpn ligand produced by decomposition was coordinated to B_{12a}. Addition of trpn to B_{12a} initially produced

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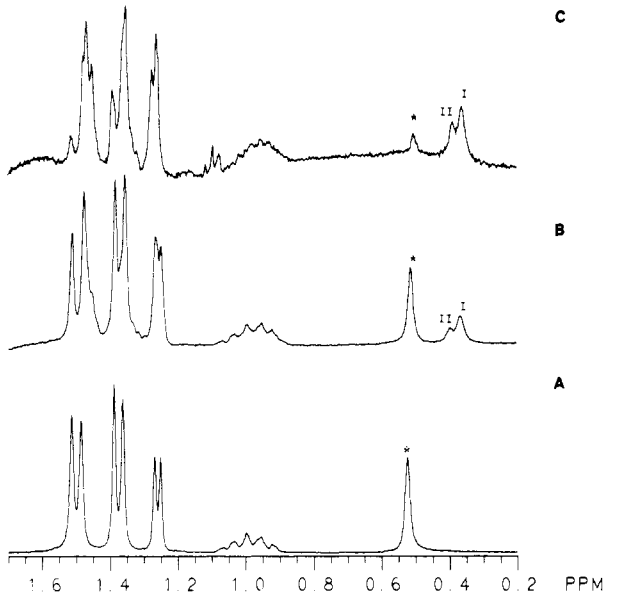

Figure 3. ^1H NMR spectra in D_2O of the upfield methyl region: (A) B_{12a}, 5 mM, pD 4.9 (designated with an asterisk); (B) solution of $[Co(trpn)(H_2O)_2]^{3+}$ and B_{12a} (4:1) [note that new species are present (signals I and II)], pD 4.9, after 8 days at room temperature; (C) solution of $[Co(trpn)(H_2O)_2]^{3+}$ and B_{12a} (12:1), pD 5, after 7 days at room temperature.

signals which are essentially identical to those of I (Table I). With time, II became more evident as observed with the $[Co(trpn)(H_2O)_2]^{3+}$ reactions. Because it is a secondary product formed after long time periods, we have not characterized II. However, some points are worthy of note. The H2 and $C20H_3$ signals are substantially shifted for both I and II into regions found with other amine ligands. Thus, we believe II is similar to I in having an axially coordinated trpn. The result for H2 rules out displacement of the coordinated 5,6-dimethylbenzimidazole for both I and II since a substantial downfield shift (below 9 ppm) would be expected.[12]

We also monitored the ^1H NMR spectra during the reaction of cyanocobalamin and $[Co(trpn)(H_2O)_2]^{3+}$. However, although $[Co(trpn)(H_2O)_2]^{3+}$ decomposed, releasing protonated trpn, even though the pD was kept at ~7, no ^1H NMR signals of either I or II were observed, even after long periods of time. This result is consistent with the axial ligation by trpn of B_{12a} since CN^- is a poorer leaving group than H_2O.

In conclusion, $[Co(trpn)(H_2O)_2]^{3+}$ is relatively unstable and tends to decompose readily under a broad range of conditions.[13] These conditions include those used previously.[3-6,13] The only new cobalamin products involve B_{12a}; the primary product formed is a simple trpn-B_{12} adduct formed by displacement of the axial aqua ligand. A secondary product, difficult to characterize because of its slow formation, probably also contains an axial coordinated trpn on the basis of the similarity in ^1H NMR shifts to the initial major product, but further studies would be necessary to characterize this minor product. However, when CNB_{12} is treated with $[Co(trpn)(H_2O)_2]^{3+}$, no evidence of the formation of I and II is found. The $[Co(trpn)(H_2O)_2]^{3+}$ complex, despite its promise as an agent to promote phosphodiester hydrolysis,[3,5] did not promote the hydrolysis of the phosphodiester group of either CNB_{12} or B_{12a}. Coordination of $[Co(trpn)(H_2O)_2]^{3+}$ to the phosphodiester group clearly does not occur, and furthermore, there is no hydrolysis of the amide groups.

Acknowledgment. A. M. Calafat is grateful to the Government of Spain for a postdoctoral Fulbright fellowship. This study was supported by NIH Grants GM 29225 and GM 29222. We thank Dr. M. Banaszczyk for helpful suggestions.

Registry No. CNB_{12}, 68-19-9; B_{12a}, 13422-52-1; trpn, 4963-47-7; $[Co(trpn)(H_2O)_2]^{3+}$, 96914-54-4; $[Co(trpn)(CO_3)]^+$, 118841-57-9.

(12) Alelyunas, Y. W.; Fleming, P. E.; Finke, R. G.; Pagano, T. G.; Marzilli, L. G. *J. Am. Chem. Soc.* **1991**, *113*, 3781-3794.

(13) The deligation reaction was noted briefly previously (Chin, J.; Kim, J. H. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 523-525), but it was not reported to occur in studies of phosphate ester hydrolysis.[3,4,6] We find decomposition occurs in the absence of B_{12} substrate. There appears to be less than 0.01 equiv of Co^{2+} present initially in our complex even after storage at ambient temperature for over 6 months as judged by the Zincon method (Rush, R. M.; Yoe, J. H. *Anal. Chem.* **1954**, *26*, 1345-1347). No detectable Co^{2+} was present in B_{12a}. The addition of 0.1 equiv of Co^{2+} had no effect on the deligation rate. The deligation appears to begin immediately after solutions are prepared, and thus any estimate of the Co^{2+} content should be high.

Contribution from the Departments of Chemistry, Yale University, New Haven, Connecticut 06511-8118, and North Carolina State University, Raleigh, North Carolina 27695-8204

Toward a Functional Model of Hydrogenase: Electrocatalytic Reduction of Protons to Dihydrogen by a Nickel Macrocyclic Complex

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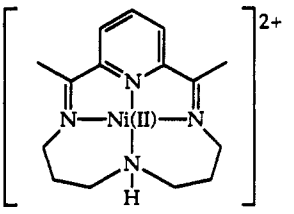
Received June 25, 1991

Functional modeling is an area of interest in bioinorganic chemistry. We have recently begun to screen a variety of Ni complexes for catalytic activity in reactions relevant to the nickel-containing metalloenzymes. For example, hydrogenases catalyze the reactions shown in eqs 1 and 2, and Ni has been

$$2H^+ + 2e^- \rightleftharpoons H_2 \quad (1)$$

$$D_2 + H_2O \rightleftharpoons HD + HOD \quad (2)$$

proposed to be the site for H_2 binding and oxidation.[1-4] We have already reported that certain Ni complexes catalyze eq 2,[5] and we now find that under electrochemical conditions, complex **1** catalyzes the physiologically important reaction shown in eq 2.



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Complex **1** is known to undergo two successive one-electron reductions.[6] In DMF solution the first couple corresponds to reduction of the ligand at −0.68 V (vs Ag/AgCl) to form a $[Ni^{II}L^{\bullet-}]^+$ species, which has been isolated and characterized by EPR spectroscopy. The second electron is delivered to the metal center at −1.25 V, to form a $[Ni^{I}L^{\bullet-}]^0$ complex. We have found that the application of an electrochemical potential of −1.1 V (pH 2.0, carbon electrode, Ag/AgCl reference) to aqueous solutions of **1** leads to visible bubbling of H_2, which is not observed in the absence of the catalyst. The potential is considerably lower than that required for the formation of the $[Ni^{I}L^{\bullet-}]^0$ complex, and the onset of catalysis results from the initial ligand-based reduction to form the $[Ni^{II}L^{\bullet-}]^+$ complex. The electrocatalytic reduction of protons to H_2 by Ni(I) has previously been observed.[7,8]

Experimental Section

Materials. Dimethylformamide (Burdick and Jackson) was used as received. Tetra-*n*-butylammonium perchlorate was purchased from

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