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

Calculations have been carried out to simulate the curves of Figure 2, assuming the mechanism described above. To perform these calculations estimates are required for the forward and backward rate constants of the rate-determining steps in reaction 1 and for the rates of reaction of the different isomers with Co(II). The forward rate constant has been determined directly and the backward rate constant can be estimated from the slope of the plot in the stopped-flow experiments described (1.35×10^{-7}) together with estimates of equilibrium constants (10^9 for isomer B and 10^{10} for isomer C compared to the literature value of 3×10^8 for the dien compound[11]). The rates of reaction 2 can be used as adjustable parameters. The values required to obtain reasonable fits are smaller than those observed in the analogous Fe^{2+} reaction by factors of 10–1000. This parallels the much slower reaction of Figure 3C rather than that of Figure 3A. The solid lines of Figure 2 result from such a calculation, employing the constants given in the caption. At times greater than 1 h the comparison should be made between the experimental data and the sum of B and C. Clearly the quality of the NMR intensity data and the overlapping of the lines do not allow for any accurate estimation of the rate parameters, but the fact that the curves can be qualitatively reproduced by using rate constants that are reasonable by the above criteria provides support for the suggested mechanism.

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Registry No. $[Co(en)(dien)Cl]^{2+}$, 33847-42-6; *ad,bet,c*-$[(Co(en)(dien))_2O_2]^{4+}$, 85281-60-3; *df,abe,c*-$[(Co(en)(dien))_2O_2]^{4+}$, 85281-59-0; O_2, 7782-44-7.

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Lewis Acidity of Cobalt(I)

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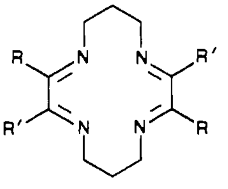
The synthesis, characterization, and reactivity of Co^{II} complexes of the macrocycles



L

are reported, where L = L^1 when R = R' = CH_3, L = L^2 when R = CH_3 and R' = Ph, and L = L^5 when R = R' = Ph. The complexes, denoted $Co^{II}L^{2+}$, undergo unusually facile one-electron reduction by a variety of reducing agents (e.g., Na/Hg, pyridine, *N*-methylimidazole) to the corresponding Co^I complexes in acetonitrile solvent. The Co^IL^+ complexes serve as potent Lewis acids toward a variety of monodentate ligands. The equilibrium constants, K_{eq}, for adduct formation between CoL^+ and the donors pyridine, 2,6-lutidine, *N*-methylimidazole, and Br^- have been measured by spectrophotometric methods and are reported herein. In general, K_{eq} increases with the donor ability of the monodentate ligand and with the electron-withdrawing ability of the macrocyclic ligand. A Lewis acid role for Co^I, which normally functions as a potent nucleophile, is highly unusual.

Introduction

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

The Co^I species typically function as Lewis bases, reacting with a variety of organic electrophiles to produce Co^{III} complexes containing the cobalt–carbon σ bond.[2-4,7,8] The possibility that Co^I might function as a Lewis acid under appropriate conditions has been mentioned only a few times in the literature. Weak coordination of a fifth ligand to Co^I occurs in vitamin B_{12s},[12] and a recent report indicates that Co^I is a better acid toward bipyridine

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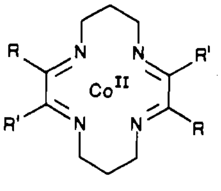
ligands than either Co^{II} or Ni^{II}.[13] However, when surrounded by a porphyrin ligand, Co^I has no tendency to bind ligands in the axial positions.[14,15] To investigate the acidity of Co^I, we have synthesized the following series of complexes, using the Co^{II} complexes (denoted CoL^{2+}) as a starting point:



CoL^{2+}

where L = L^1 when R = R′ = CH_3, L = L^2 when R = CH_3 and R′ = Ph, and L = L^5 when R = R′ = Ph. We chose these macrocyclic ligands because they contain the bis(α-diimine) structural feature, known to stabilize Co^I.[7,13,16] It was our expectation that the ligand L^5 might prove particularly effective in promoting Lewis acidity of Co^I, since the electron-withdrawing phenyl substituents on the imine carbons should lower the imine π^* orbital energies. This expectation has been borne out. Using a combination of electrochemical and spectroscopic methods, we have uncovered some interesting cobalt chemistry.

1. CoL^+[17] becomes increasingly stable relative to CoL^{2+} as the imine substituents of the macrocycle, L, are changed from CH_3 to C_6H_5.

2. $E_{1/2}{}^{CoL^{2+}-CoL^+}$ for the complexes ranges from −0.36 V for $(CoL^1)^{2+}$ to −0.07 V for $(CoL^5)^{2+}$ vs SCE in acetonitrile. The latter is the most positive value yet found for the $Co^{II/I}$ couple. Consistent with their positive $E_{1/2}$ values, all three Co^{II} complexes (L = L^1, L^2, L^5) undergo reduction to CoL^+ by aromatic N-heterocycles such as pyridine and *N*-methylimidazole, which normally coordinate to Co^{II} without reducing it.

3. The CoL^+ complexes are strong Lewis acids toward a variety of ligands in acetonitrile. They are stronger acids than the analogous $(Co^{II}L)^{2+}$ or $(Ni^{II}L)^{2+}$ complexes, in agreement with the trend reported elsewhere.[13]

4. Only one molecule of Lewis base binds axially to CoL^+, according to (1). K_{eq} values for adduct formation follow the

$$CoL^+ + B \rightarrow CoL(B)^+ \tag{1}$$

ordering given below. For L, $CoL^5 > CoL^2 > CoL^1$, consistent with the electron-withdrawing abilities of the substituents on L; for B, *N*-methylimidazole > pyridine > Br^- > 2,6-lutidine, consistent with the donor abilities of these ligands.

The values of K_{eq} for (1) are in the range $10-10^5$, indicating an unexpectedly high acidity for the CoL^+ complexes. Possible reasons for this will be discussed.

Experimental Section

Reagents. Reagent grade acetonitrile (An) (Baker) was refluxed over phosphorus pentoxide for 24 h under nitrogen and distilled under nitrogen. Reagent grade pyridine (py) (Baker) and 2,6-lutidine (lut) were refluxed over potassium hydroxide for 24 h under nitrogen and distilled under nitrogen. *N*-Methylimidazole (MeIm) was refluxed over potassium hydroxide for 2 h under reduced pressure and distilled under reduced pressure. 2,6-di-*tert*-butylpyridine (DTBP) (Aldrich, 97%) and sodium and mercury metals were used without further purification. All other materials were reagent grade and were used as received.

Syntheses. $[CoLBr_2]Br$. Literature methods were used for the preparation of the three dibromocobalt(III) bromide complexes, in which L = L^1,[18] L^2,[19,20] and L^5.[21]

$[CoL(An)_2](ClO_4)_3$. These complexes were prepared as described elsewhere.[22]

$[CoL(An)_2](BPh_4)_2$. These complexes, with L = L^1, L^2, L^5, were synthesized by the following general procedure. $CoL(An)_2(ClO_4)_3$ (typically 1–2 g) was slurried with An/ethanol (1/1) (typically 120 mL), and the slurry was refluxed until the solid dissolved and a deep red solution was obtained (10 h). Filtration, followed by addition of sodium tetraphenylborate (2 mol/mol of Co) to the filtrate, afforded violet crystals of $CoL(An)_2(BPh_4)_2$. The product was collected, washed with anhydrous ether, recrystallized from An in an inert-atmosphere glovebox (vide infra), and characterized by elemental analysis and electronic absorption, IR, and EPR spectroscopy.

Anal. Calcd for $CoL^1(An)_2(BPh_4)_2$ ($C_{66}H_{70}N_6B_2Co$): C, 77.12; H, 6.86; N, 8.18; Co, 5.73; B, 2.10. Found: C, 77.09; H, 7.01; N, 8.11; Co, 5.86; B, 2.09.

Anal. Calcd for $CoL^2(An)_2(BPh_4)_2$ ($C_{76}H_{74}N_6B_2Co$): C, 79.24; H, 6.47; N, 7.29; Co, 5.12; B, 1.88. Found: C, 79.24; H, 6.60; N, 7.09; Co, 5.14; B, 1.95.

Anal. Calcd for $CoL^5(An)_2(BPh_4)_2$ ($C_{86}H_{78}N_6B_2Co$): C, 80.94; H, 6.16; N, 6.59; Co, 4.62; B, 1.69. Found: C, 80.85; H, 6.40; N, 7.02; Co, 4.51; B, 1.49.

$[CoL](BPh_4)$. These complexes were prepared by two methods, both carried out in the inert-atmosphere glovebox. In the first, ~10 mL of a ~10^{-3} M solution of $[CoL(An)_2](BPh_4)_2$ in An was stirred over 2 g of 1% sodium amalgam (Na/Hg) until the color of the solution had changed from purple to blue. The excess Na/Hg was then removed and the solution of $[CoL](BPh_4)$ (which contained 1 mol of $NaBPh_4$/mol of Co) was characterized by electronic absorption spectroscopy and cyclic voltammetry and in the case of L^1 by Evans method[23] magnetic susceptibility measurements. Removal of solvent from a solution of $[CoL^1](BPh_4)$ produced via reduction with Na/Hg resulted in a blue solid. Attempts to obtain an elemental analysis of the highly oxygen-sensitive solid produced widely varied results.

Prolonged exposure (>20 min) of solutions of $[CoL](BPh_4)$ to Na/Hg resulted in further reduction to produce intensely green solutions. These solutions were not characterized.

The tendency for reaction between Na/Hg and CoL^{2+} to proceed past the desired point made this synthetic route somewhat unpredictable. Clearly, incorrect reaction time would yield a product contaminated either with CoL^{2+} or CoL. That we frequently detect paramagnetism in solutions of $(CoL^1)^+$ produced by Na/Hg reduction is consistent with either possibility. To avoid these problems, solutions of $[CoL](BPh_4)$ for Lewis acidity studies were prepared by a second method.

In the second method, 25 mL of a 10^{-3} M solution of $[CoL(An)_2](BPh_4)_2$ containing 0.1 M Bu_4NClO_4 was subjected to controlled-potential electrolysis (CPE) at an appropriate potential (−0.60 V vs. aqueous SCE for L = L^1; −0.50 V for L = L^2; −0.35 V for L = L^5) until the electrolysis current had fallen to 1% of its initial value. The resulting blue solutions of $[Co^IL](BPh_4)$ were characterized by electronic absorption spectroscopy, EPR spectroscopy, and cyclic voltammetry. The electronic spectra were identical with those of solutions of $[Co^IL](BPh_4)$ produced via reduction with Na/Hg. However, the CPE method of synthesis produces solutions whose resting electrical potentials are in the plateau region negative of the potential at which the CV wave for the $CoL^{2+}-CoL^+$ couple occurs. This insures that negligible amounts of CoL^{2+} or CoL^0 are present in solution.

1% Sodium Amalgam. Sodium (0.2 g) was cut into small pieces, washed with hexane, and added to 20 g of mercury under dry nitrogen. The resulting amalgam was stored in the glovebox.

Reactions of $CoL(An)_2{}^{2+}$ with B (B = py, MeIm, lut, DTBP). Reactions of $(Co^{II}L)^{2+}$ with the indicated Lewis bases, B, were carried out in An solvent in the glovebox. Electronic spectral studies confirm that the products are $(CoL)^+$ containing coordinated B (1 mol/mole of Co). These reactions will be discussed fully in the Results section.

Physical Methods. To exclude oxygen, all solutions for characterization or reaction were prepared in a Vacuum Atmospheres HE-43-1 DriLab equipped with a MO-40-IV purification train, with N_2 used as

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(17) Here the symbol $(CoL)^{n+}$ is used to indicate that the CoL moiety carries a positive charge of *n* units without specifying the oxidation state of cobalt. The oxidation state will be specified by a superscript Roman numeral, as follows: $Co^{II}L^{2+}$ = 2+ complex with cobalt in the II oxidation state. Further, we will assume axially coordinated solvent (An) to be implicit in the symbol CoL. At present we have no knowledge of extent of axial coordination by solvent in the CoL^+ species.

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Table I. Electronic Spectral and Magnetic Data in Acetonitrile Solvent

complex	λ_{max}, nm	$10^{-3}\epsilon$, M^{-1} cm^{-1}	μ_{eff}, μ_B
$(CoL^1)^{2+}$	358	1.4	1.74
	505	3.5	
	520	3.6	
$(CoL^2)^{2+}$	368	1.9	
	538	4.9	
$(CoL^5)^{2+}$	553	6.5	
$(CoL^1)^+$	750	6.8	0.87
	630	5.2	
	530	3.6	
	394	1.7	
$(CoL^2)^+$	750	9.5	
	620	6.4	
	540	5.2	
$(CoL^5)^+$	750	10.3	
	610	6.3	
	545	5.8	
$(CoL^1py)^+$	750	6.8	
	595	4.1	
	525	5.0	
	414	4.3	
$(CoL^1MeIm)^+$	750	7.3	
	590	3.9	
	530	4.8	
	400	1.7	
$(CoL^2py)^+$	750	9.5	
	595	5.3	
	530	6.9	
	410	4.3	
$(CoL^2MeIM)^+$	750	11.6	
	590	5.0	
	530	7.2	
	400	2.3	
$(CoL^5py)^+$	750	11.3	
	595	4.9	
	530	7.5	
	405	4.3	
$(CoL^5MeIM)^+$	750	12.2	
	530	7.7	

the inert gas. Unless otherwise indicated, An was used as the solvent for all studies.

Elemental Analyses. Analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

Spectroscopy. Electronic absorption spectra were obtained with a Perkin-Elmer 553 UV-vis spectrophotometer and Model 561 recorder. Absorbances at fixed wavelength were measured in the glovebox by using a Sequoia-Turner Model 340 spectrophotometer. EPR spectra were obtained with a Varian E-9 spectrometer operating at X-band frequencies. IR spectra were obtained from KBr pellets and/or Nujol mulls by using a Perkin-Elmer 683 infrared spectrometer and PE 3600 data station.

Spectrophotometric Titrations. To determine the stoichiometry and equilibrium constant for (1), spectrophotometric titrations of solutions of $(CoL)^+$ with B (B = py, MeIm, lut, Br^-) were performed in two ways. In the first, aliquots of B were added through a serum cap to a solution $\sim 10^{-4}$ M in CoL^+, contained in a 1-cm spectrophotometer cell, and the electronic spectrum was scanned between 750 and 250 nm after each addition. Titrations were performed in this manner to detect isosbestic points. In the second method, absorbance was read at a single appropriate wavelength after each addition of B by using a spectrophotometer in the glovebox. This avoided contamination by small amounts of O_2, which occasionally occurred with the first method. The data from such titrations allowed determination of the stoichiometry and equilibrium constant for (1) via the appropriate plot of (2).[24] Here A_0 is the absorbance of a solution of pure CoL^+, A_∞ is the absorbance of a solution containing the same concentration of pure $CoL(B)_q^+$, A is the absorbance of a solution containing both CoL^+ and $CoL(B)_q^+$ in amounts dictated by [B] and K_{eq}, q is the number of moles of B that coordinate to CoL^+, [B] is the concentration of free B, and K_{eq} is the equilibrium constant for (1). In all cases, plots of the left side of (2) versus ln [B] were linear with a slope near 1, consistent with the stoichiometry reported in (1).

$$\ln\left(\frac{A_0 - A}{A - A_\infty}\right) = q \ln [B] + \ln k_{eq} \qquad (2)$$

Electrochemistry. Cyclic voltammetry (CV) was performed by using a PAR 373 potentiostat-galvanostat with a PAR 175 universal programmer and a Houston Instruments 2000 X-Y recorder. The usual three-electrode configuration was used with a two-compartment cell. The counter and working electrodes (Pt wire and Pt button, respectively) were placed in the working solution containing $\sim 5 \times 10^{-4}$ M $Co^{III}L^{2+}$ and 0.1 M tetrabutylammonium perchlorate (TBAP). This was separated by sintered frit from the reference compartment, consisting of an aqueous saturated calomel electrode immersed in an An solution of 0.1 M TBAP. A scan rate of 200 mV/s was typically used. $E_{1/2}$ values given in Table II were calculated as the average of the anodic and cathodic peak potentials (E_p^a and E_p^c, respectively) of the cyclic voltammogram for the couple. Controlled-potential electrolysis (CPE) was carried out by using the same equipment and a modified electrode configuration. The counter electrode was placed in the reference compartment with the SCE, and a platinum grid was used as the working electrode. Electrolyses were carried out at appropriate plateau potentials and were continued until the current had fallen to about 1% of its initial value. The number of electrons involved in the electrode process was determined by integration of the current-time data.

Electrochemical Titrations. These were performed to determine the effect of added Lewis base on the position of the cyclic voltammogram for the CoL^{2+}–CoL^+ redox couple. Typically, successive aliquots of Lewis base were added to the working compartment of the cell and the cyclic voltammogram of the CoL^{2+}–CoL^+ couple was recorded after each addition. The direction of the shift in $E_{1/2}$ was used to deduce the relative Lewis acidities of CoL^{2+} and CoL^+ toward the added Lewis base.[25]

Magnetic Susceptibility. Magnetic susceptibilities were measured by using the Evans NMR method.[23] An containing 10 vol% benzene was used as the solvent. Mass susceptibilities were calculated from the difference in position of the benzene resonance in the presence and absence of the compound of interest. Molar susceptibilities were corrected for diamagnetism by using Pascal's constants.[26] Susceptibilities of the CoL^+ species were determined by using solutions prepared by Na reduction to avoid correcting for a large concentration of electrolyte.

Results and Discussion

Synthesis and Characterization of the Complexes [CoL]$(BPh_4)_2$. All three complexes are readily synthesized by the ethanol reduction procedure reported earlier for $(CoL^1)^{2+}$.[27] The complexes are obtained as the tetraphenylborate salts by addition of $NaBPh_4$ to a concentrated solution of the complex in An. Elemental analyses indicate two An molecules per cobalt for all three complexes in the solid state. Infrared spectra of the compounds are similar, with the expected absorptions at 3050–2940, 700, and 610 cm^{-1} due to BPh_4^-;[28] at 2200–2300 cm^{-1} due to An;[29] and at 1200–1250 cm^{-1} due to the α-diimine function of the macrocyclic ligand.[18] EPR spectra of frozen An solutions of the complexes are typical of low-spin tetragonal $Co^{II}(e_g^4\ b_{2g}^2\ a_{1g}^1)$.[27,30] Specifically, $g_\perp > g_\parallel$, with the parallel branch split into eight components due to hyperfine coupling with the Co nucleus ($I = {}^7/_2$). For $(CoL^1)^{2+}$, a five-line superhyperfine structures is seen, indicating that the complex is six-coordinate in An. In contrast, both $(CoL^5)^{2+}$ and $(CoL^2)^{2+}$ exhibit three-component superhyperfine structure, consistent with only one axially coordinated An molecule. This unexpected result is discussed elsewhere.[19] Each of

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Table II. Cyclic Voltammetric Data for Macrocyclic Ligand Complexes of Cobalt(II) vs Aqueous SCE

complex	$E_{1/2}^{\mathrm{Co(II/I)}}$	$E_{1/2}^{\mathrm{Co(III/II)}}$	other redns	solvent	ref
$\mathrm{CoTPP(DMF)}_x$[a]	−0.77	0.300		DMF	31
Co(*p*-Cl)TPP[b]	−0.78				31
$\mathrm{CoTPP(DMSO)}_x$	−0.814	0.130		DMSO	31, 32
Co(*p*-CH_3)TPP[b]	−0.84				31
Co(*p*-OCH_3)TPP[b]	−0.86				31
$\mathrm{CoTPP(benzonitrile)}_x$	−0.86	0.486		benzonitrile	31
CoPROTO[c]	−0.96				33, 34
$\mathrm{CoTPP(py)}_x$	−1.03	−0.214		pyridine	31
CoETIO[d]	−1.04				35
CoOEP[e]	−1.05				36, 37
$\mathrm{CoL^5(An)_2}^{2+}$	−0.07	0.684[f]	−0.973	An	this work
			−1.305	An	
$\mathrm{CoL^2(An)_2}^{2+}$	−0.194	0.52[f]	−1.088	An	this work
$\mathrm{CoL^1(An)_2}^{2+}$	−0.350	0.445	−1.206	An	this work, 16
$\mathrm{Co(Me_2[14]py\text{-}dieneN_4)}^{2+}$[g]	−0.50	0.53		An	16
$\mathrm{Co(Me_2[14]\text{-}1,3\text{-}dieneN_4)}^{2+}$[g]	−0.81	0.41		An	16
$\mathrm{Co(Me_6[14]\text{-}1,4,8,11\text{-}tetraeneN_4)}^{2+}$[g]	−0.96	0.49		An	16
$\mathrm{Co(Me_6[14]\text{-}4,11\text{-}dieneN_4)}^{2+}$[g]	−1.33	0.49		An	16
$\mathrm{Co(Me_6[14]\text{-}4,14\text{-}dieneN_4)}^{2+}$[g]	−1.33	0.49		An	16
$\mathrm{Co(Me_2[14]py\text{-}aneN_4)}^{2+}$[g]	−1.36	0.47		An	16
$\mathrm{Co(Me_4[14]\text{-}1,8\text{-}dieneN_4)}^{2+}$[g]	−1.38	0.36		An	16
$\mathrm{Co(Me_2[14]\text{-}1\text{-}eneN_4)}^{2+}$[g]	−1.50	0.44		An	16
$\mathrm{Co(Me_2[14]aneN_4)}^{2+}$[g]	−1.67	0.27		An	16
$\mathrm{Co(Me_6[14]aneN_4)}^{2+}$[g]	−1.85	0.44		An	16

BPh_4^- gives an irreversible oxidation wave at 0.8 V vs SCE

[a] TPP = tetraphenylporphyrinate(2−). [b] (*p*-Cl)TPP = tetrakis(*p*-chlorophenyl)porphyrinate(2−). [c] PROTO = protoporphyrinate(2−). [d] ETIO = etioporphyrinate(2−). [e] OEP = octaethylporphyrinate(2−). [f] Obscured by BPh_4^- oxidation, confirmed by CV of $NaBPh_4$ in An. [g] Originally measured vs Ag/Ag^+ (0.1 M) reference electrode. Values converted to SCE reference by adding 0.36 V to the Ag/Ag^+ (0.1 M) values.

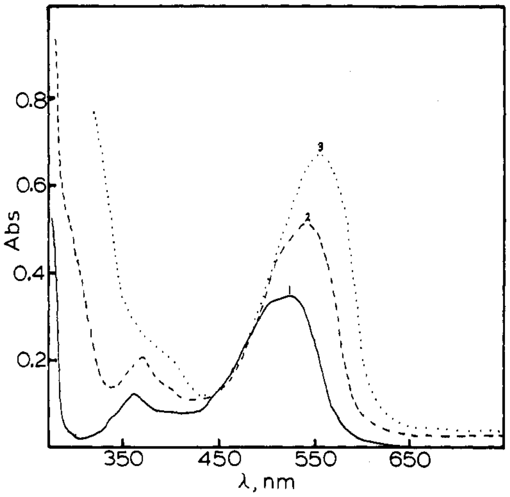

Figure 1. Electronic absorption spectra of 1.0 × 10^{-4} M CoL^{2+} in acetonitrile: (1) $(CoL^1)^{2+}$; (2) $(CoL^2)^{2+}$; (3) $(CoL^5)^{2+}$.

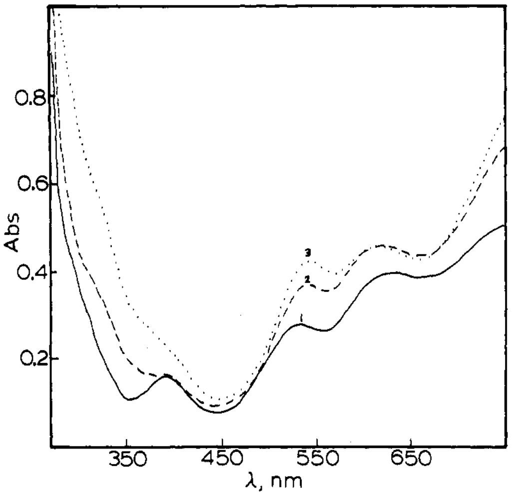

Figure 2. Electronic absorption spectra of 0.72 × 10^{-4} M CoL^+ in acetonitrile: (1) $(CoL^1)^+$; (2) $(CoL^2)^+$; (3) $(CoL^5)^+$.

the complexes exhibits an intense electronic absorption band at 500–550 nm in An solvent, resulting from metal-to-ligand charge transfer. The spectra of the complexes are shown in Figure 1, and the absorption maxima and extinction coefficients are collected in Table I. For $(CoL^1)^{2+}$, the effective magnetic moment calculated from the corrected susceptibility is consistent with one unpaired electron per cobalt (Table I). Finally CV of An solutions of the complexes gave reversible waves (ΔE_p = ~70 mV) for the CoL^{2+}–CoL^+ couple, and for the CoL^{2+}–CoL^{3+} couple in the case of L^1. Further reversible waves were seen at more negative potentials. $E_{1/2}$ values for the complexes are given in Table II, which also includes electrochemical data for a representative collection of cobalt macrocyclic ligand complexes.

Several observations about the electrochemical data may be made. First, $E_{1/2}(CoL^{2+}$–$CoL^+)$ becomes more positive as the electron-withdrawing ability of the imine substituents of L increases ($(CH_3)_4 < (CH_3)_2Ph_2 < Ph_4$). The total shift in $E_{1/2}$ resulting from replacement of four methyl by four phenyl groups is 0.28 V, or about 70 mV per phenyl group. Second, the range of $E_{1/2}$ values spanned by the complexes in Table II is remarkable. The complex $\mathrm{Co^{II}(Me_6[14]aneN_4)(An)_2}^{2+}$, in which the macrocyclic ligand is fully saturated and unable to π bond with the metal, is reduced at −1.85 V vs SCE. In contrast, $(CoL^5)^{2+}$ is reduced at a very mild −0.07 V vs SCE. Thus, by a simple variation of the macrocyclic ligand structure, the CoL^{2+}–CoL^+ redox potential can be tuned through a range of 1.8 V. The variation available with porphyrin ligands is only 0.24 V for the compounds included in the table. Third, $E_{1/2}(CoL^{2+}$–$CoL^+)$ for $(CoL^5)^{2+}$ is the most positive yet found for a macrocyclic ligand complex of cobalt, consistent with the electron-withdrawing ability of L^5.[38]

Synthesis and Characterization of the Complexes CoL^+. The CoL^+ complexes were prepared from CoL^{2+} either by reduction with Na/Hg or by electrolysis at fixed potential, as described in the Experimental Section. Coulometry during electrolysis confirms that reduction is by one electron. The electronic spectra of the CoL^+ species are shown in Figure 2. Identical spectra were obtained for a given complex by either synthetic method. Ab-

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(38) Kildahl, N. K.; Antonopoulos, G.; Fortier, N. E.; Hobey, W. D. *Inorg. Chem.* **1985**, *24*, 429.

sorption maxima and extinction coefficients are collected in Table I.

Frozen solutions of $\mathrm{CoL^+}$ synthesized via Na/Hg reduction are either EPR inactive or show weak signals probably attributable either to unreduced $\mathrm{CoL^{2+}}$ or to $\mathrm{CoL^0}$, a product of reduction by two electrons. Consistent with these weak EPR signals, the Evans NMR method shows very small bulk shifts resulting from a slight paramagnetism for $\mathrm{(CoL^1)^+}$. The effective magnetic moment calculated from these shifts and based on the $\mathrm{CoL(BPh_4)}$ formulation is given in Table I. The very small shifts observed (~0.5 Hz) and the substantial error in the diamagnetic correction for these high molecular weight species contribute to a large uncertainty in calculated paramagnetic susceptibilities. The value in Table I is therefore approximate.

Finally, cyclic voltammograms of solutions of $\mathrm{CoL^+}$ are identical with those of the parent $\mathrm{CoL^{2+}}$ complexes (Table II).

Having presented the characterizational data for the $\mathrm{CoL^{2+}}$ complexes and their one-electron-reduction products, $\mathrm{CoL^+}$, we will consider the question of the electronic structure of the latter. Three possible products of one-electron reduction of $\mathrm{Co^{II}L^{2+}}$ may be considered: $\mathrm{Co^IL^+}$ (reduction at the metal); $\mathrm{Co^{II}(L^{\bullet-})^+}$ (reduction at the macrocycle); and $\mathrm{Co^{III}\,(L^{2-})}$ (one-electron reduction at either the metal or the macrocycle, followed by internal electron transfer from metal to macrocycle). There is precedent for each of these possibilities. Addition of one electron to $\mathrm{Fe(Me_6[14]\text{-}1,3,8,10\text{–}tetraene\ N_4)^{2+}}$, in which the macrocycle is very similar to $\mathrm{L^1}$, occurs at the metal to produce a complex of $\mathrm{Fe^I}$.[39] In contrast, addition of one electron to $\mathrm{(Ni^{II}L^1)^{2+}}$ occurs at the ligand to produce a nickel(II) anion radical species.[40] Finally, one-electron reduction of $\mathrm{Co^{II}TAAB^{2+}}$ results initially in a $\mathrm{Co^I}$ complex, which then undergoes internal electron transfer to produce $\mathrm{Co^{III}(TAAB^{2-})^+}$.[41] Clearly, then, each of these possibilities deserves serious consideration. The results discussed above can be used to make a choice, as follows.

1. The electronic spectra of $\mathrm{CoL^+}$, L = $\mathrm{L^1}$, $\mathrm{L^2}$, and $\mathrm{L^5}$, in An are very similar to the spectrum of $\mathrm{(Co^IL^1)^+}$ in aqueous solution, determined from pulse-radiolysis experiments.[42] The distinctive feature is an intense band near 700 nm. Further, the spectra of $\mathrm{CoL^+}$ are similar to that of $\mathrm{(Co^ITAAB)^+}$ but markedly different from that of $\mathrm{Co^{III}(TAAB^{2-})^+}$.[41] The electronic spectral evidence thus supports reduction at the metal.

2. The one-electron reduction of $\mathrm{Co^{II}L^{2+}}$ is electrochemically reversible. This argues strongly against the $\mathrm{Co^{III}(L^{2-})}$ formulation since this species can be formed only by internal electron transfer following the initial one-electron reduction of either metal or ligand. Indeed, $\mathrm{Co^{III}(TAAB^{2-})^+}$, the ultimate product of one-electron reduction of $\mathrm{Co^{II}TAAB^{2+}}$, undergoes oxidation at a potential far positive of both the potential for reduction of $\mathrm{Co^{II}TAAB^{2+}}$ and the potential for oxidation of $\mathrm{Co^ITAAB^+}$.[41] We have found that the $\mathrm{CoL^+}$ species are stable in An solution for months in the absence of oxygen and that their cyclic voltammograms are identical with those of the $\mathrm{Co^{II}}$ complexes. Further, controlled-potential electrolyses of $\mathrm{CoL^+}$ at a potential positive of $E_{1/2}(\mathrm{CoL^+\text{–}CoL^{2+}})$ regenerates $\mathrm{CoL^{2+}}$, as judged by the electronic spectrum. These observations argue strongly against the $\mathrm{Co^{III}(L^{2-})^+}$ formulation.

3. As we will show shortly, the $\mathrm{CoL^+}$ complexes are strong Lewis acids. This is inconsistent with the $\mathrm{Co^{II}(L^{\bullet-})}$ formulation. There is no reason to expect the acidity of $\mathrm{Co^{II}}$ to be dramatically increased by reduction of the macrocyclic ligand. In fact, acidity should be decreased by a negative charge on the macrocycle.

The potent Lewis acidity is most consistent with the $\mathrm{Co^{III}(L^{2-})^+}$ formulation. However, this formulation is convincingly ruled out by electronic spectral and electrochemical results. As will be seen, it is possible to rationalize the acidity in terms of the $\mathrm{Co^IL^+}$ formulation in a couple of ways.

4. Finally, one-electron reductions of a variety of metal complexes of $\mathrm{L^1}$ result in ligand reduction in only one case, that of $\mathrm{(Ni^{II}L^1)^{2+}}$ cited earlier. Both $\mathrm{(Cu^{II}L^1)^{2+}}$[28] and $\mathrm{(Fe^{II}L^1)^{2+}}$[39] undergo reduction at the metal. Reduction of the nickel complex occurs at the ligand most probably because the lowest unoccupied metal orbital is the strongly antibonding $d_{x^2-y^2}$. In $\mathrm{(Cu^{II}L^1)^{2+}}$, this orbital is already singly occupied, indicating that it is of lower energy than the ligand LUMO. In both $\mathrm{(Fe^{II}L^1)^{2+}}$ and $\mathrm{(Co^{II}L^1)^{2+}}$, a relatively low energy metal orbital (d_{z^2}) is available.

The small paramagnetism of $\mathrm{(CoL^1)^+}$ synthesized by Na/Hg reduction is consistent with any of the following possibilities: (a) $\mathrm{Co^IL^+}$ containing a small quantity of high-spin $\mathrm{Co^I}$; (b) $\mathrm{Co^IL^+}$ containing a small quantity either of residual $\mathrm{CoL^{2+}}$ or of $\mathrm{(CoL)^0}$; (c) $\mathrm{Co^{II}(L^{\bullet-})^+}$ in which the two odd electrons, one on the ligand and one on cobalt, are antiferromagnetically coupled; (d) $\mathrm{Co^{III}(L^{2-})}$ containing a small quantity either of residual $\mathrm{CoL^{2+}}$ or of $\mathrm{CoL^0}$. The magnetic results do not provide strong support for any of the three possible formulations.

All things considered, the experimental evidence supports the $\mathrm{Co^IL^+}$ alternative most strongly. In the ensuing discussion it will be assumed that this is the correct formulation.

Reaction of $\mathrm{Co^{II}L^{2+}}$ with B (B = py, MeIm, Lut, DTBP). Addition of excess py or MeIm to an An solution of any of the three $\mathrm{Co^{II}L^{2+}}$ complexes results in reduction of $\mathrm{Co^{II}L^{2+}}$ to $\mathrm{Co^IL^+}$ and coordination of B to the $\mathrm{Co^I}$ center, according to (3). With

$$\mathrm{Co^{II}L + 2B \rightarrow Co^ILB + B^{ox}} \qquad (3)$$

the exception of the reaction of $\mathrm{(Co^{II}L^1)^{2+}}$ wity py, which is incomplete, electronic spectra of the product solutions are identical with those of the adducts of $\mathrm{Co^IL^+}$ and B, produced by addition of B to $\mathrm{Co^IL^+}$ (vide infra, Table I). The product solutions are EPR inactive and diamagnetic, according to the NMR susceptibility studies. Reaction 3 appears unusual, in that py and MeIm normally react with $\mathrm{Co^{II}}$ complexes only via axial substitution. In fact, (3) is a simple consequence of the unusually positive values of $E_{1/2}$ for the $\mathrm{CoL^{2+}\text{–}CoL^+}$ couple and the stabilization provided by formation of the adduct, $\mathrm{Co^IL(B)^+}$ (vide infra).

According to (3), it is the aromatic heterocycle, py or MeIm, that reduces $\mathrm{Co^{II}L^{2+}}$. There are several other possibilities. First, the aromatic heterocycle might react with a small amount of $\mathrm{H_2O}$ present in the solvent to produce $\mathrm{OH^-}$, which might then function as the reducing agent. In order to test this possibility, we carried out several experiments.

1. Water was added to the reaction solution at concentrations up to 0.5 M. The initial rate of (3)[43] was independent of the concentration of added water, which argues against the $\mathrm{OH^-}$ pathway.

2. Sterically hindered aromatic heterocycles, 2,6-lutidine and 2,6-di-*tert*-butylpyridine, were reacted with $\mathrm{Co^{II}L^{2+}}$. If the reduction to $\mathrm{CoL^+}$ occurs according to (3), requiring coordination of B to $\mathrm{Co^{II}L^{2+}}$, the rate of reduction should be a function of the oxidizability of B, which is expected to decrease in the order DTBP > lut > py. This ordering is based upon substituent donor abilities. On the other hand, if the function of B is as a Bronsted–Lowry base toward $\mathrm{H_2O}$, the rate of reduction should be higher with lut and py than with DTBP, in a manner that parallels the $\mathrm{p}K_\mathrm{a}$ values of the species (lut (5.77) > py (4.38) > DTBP (3.58) in ethanol/$\mathrm{H_2O}$ (1:1), and lut(6.75) > py (5.17) in $\mathrm{H_2O}$).[44] We observe that the initial rates of reduction stand in the following order:[43]

$$\underset{16}{\text{lut}} > \underset{6}{\text{py}} > \underset{1}{\text{DTBP}}$$

The ordering is more consistent with a Bronsted–Lowry role for B than with the scheme in (3), although the total range of rates spans only one order of magnitude.

3. Cyclic voltammetry was performed in an attempt to find hydrogen peroxide, a likely product of a process in which $\mathrm{OH^-}$ is oxidized. No evidence for $\mathrm{H_2O_2}$ was found. On the basis of

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[39] Dabrowiak, J. C.; Lovecchio, F. V.; Goedkin, V. L.; Busch, D. H. *J. Am. Chem. Soc.* **1972**, *94*, 5502.

[40] Lovecchio, F. V.; Gore, E. S.; Busch, D. H. *J. Am. Chem. Soc.* **1974**, *96*, 3109.

[41] Takvoryan, N.; et al. *J. Am. Chem. Soc.* **1974**, *96*, 731.

[42] Tait, A. M.; Hoffman, M. Z.; Hayon, E. *J. Am. Chem. Soc.* **1976**, *98*, 86.

[43] Kildahl, N.; Viriyanon, P., unpublished results.

[44] Brown, H. C.; Kanner, B. *J. Am. Chem. Soc.* **1966**, *88*, 986.

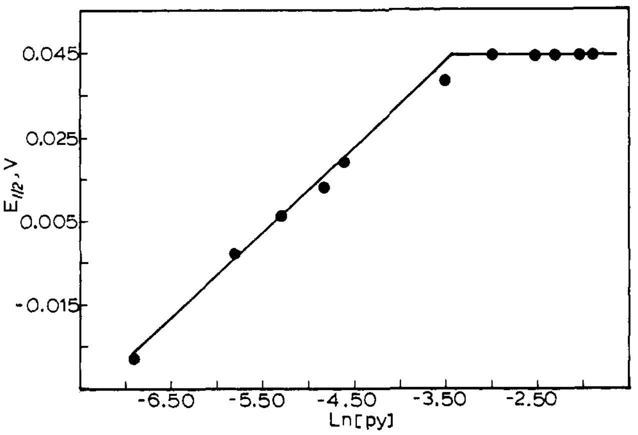

Figure 3. Plot of $E_{1/2}$ vs. ln $[py]_{tot}$ for the electrochemical titration of $(CoL^5)^{2+}$ with pyridine.

these experiments, we conclude that OH^- is not functioning as the reducing agent in these systems. The most convincing support for this conclusion is the lack of a rate dependence on the concentration of added water. Second, it is known that in basic solution, α-diimine complexes of Co^{II} undergo disproportionation to the corresponding Co^{III} and Co^{I} complexes.[12] Such a reaction, however, must necessarily involve OH^- in some capacity. It therefore seems unreasonable for the rate to be independent of the concentation of added water. This pathway, too, seems to be ruled out by our observations. Third, BPh_4^- is known to serve as a reducing agent[45] and recently has been implicated in the reduction of $(Cu^{II}L^1)^{2+}$ in acetone.[28] Indeed, we observe an oxidation wave for BPh_4^- in the cyclic voltammogram for the complexes at ~0.8 V vs. SCE (Table II). The anion is thus expected to serve as a reducing agent for species with reduction potentials in the range >~0.7 V. However, it is clear from our work with the $Co^{III}L(ClO_4)_3$ salts that BPh_4^- is not responsible for reduction of CoL^{2+} to CoL^+. The cyclic voltammogram of $Co^{III}L^5(ClO_4)_3$ is identical with that of $CoL^5(BPh_4)_2$, with the exception that the BPh_4^- wave is absent in the former. Addition of py to a solution of $[Co^{III}L^5](ClO_4)_3$ results in reduction first to CoL^{2+} and then more slowly to CoL^+. The electronic spectrum of the final solution is identical with that of a solution of $CoL^5(py)^+$. Finally, controlled-potential electrolysis of a solution of $(CoL^1)(ClO_4)_3$ at -0.60 V vs SCE produces a blue solution with electronic spectrum identical with that produced by reduction of $(Co^{II}L^1)(BPh_4)_2$. Addition of B produces spectra identical with those resulting from (3). We conclude, then, that reduction of $Co^{II}L^{2+}$ in the presence of B occurs according to (3).

The relative initial rates of (3) exhibit the following patterns:[43] $CoL^5 > CoL^2 > CoL^1$ for same B; MeIm > py > lut > 2,6-DTBP for same L. The patterns are entirely consistent with the $E_{1/2}$-$(Co^{II/I})$ values for the complexes ($E_{1/2}(CoL^1) < E_{1/2}(CoL^2) < E_{1/2}(CoL^5)$), the relative reducing abilities of the unhindered donors py and MeIm, and the steric requirements of the series of pyridine donors, respectively.

Finally, the identity of B^{ox}, the oxidation product of B, has not been established. However, the absence of an EPR spectrum for product solutions from (3) indicates that the ultimate product is not a radical.

Lewis Acidity of CoL^+. Electrochemical Titration of $Co^{II}L^{2+}$ with B (B = py and MeIm). Titration of a solution of $(Co^{II}L^5)^{2+}$ with py in An results in a positive shift of the $Co^{II/I}$ wave, by 0.112 V, until [py] = 0.05 M, after which no further shift occurs. A plot of $E_{1/2}$ vs ln [py] is shown in Figure 3. Similar positive shifts are observed upon addition of either py or MeIm to any of the Co^{II} complexes. The direction of the shift in $E_{1/2}$ is surprising, because it indicates that the acidity of CoL^+ exceeds that of CoL^{2+}. This contrasts with the situation for cobalt porphyrins (P), for example, in which no interaction of Co^IP with potential axial ligands can be detected.[14] The Lewis acidity of the CoL^+ complexes is readily studied by using electronic spectral methods. The results of such studies will now be discussed.

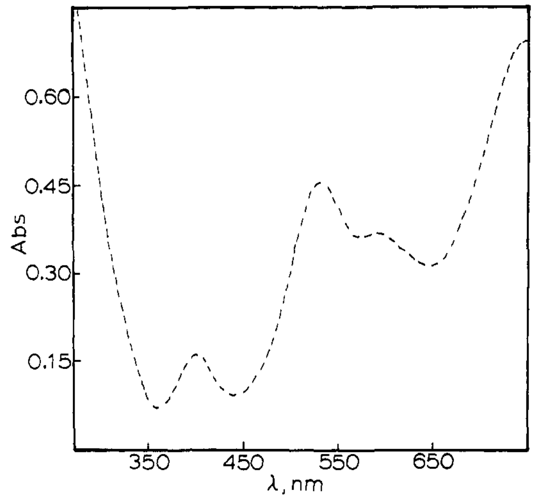

Figure 4. Electronic absorption spectrum of $CoL^1(MeIm)^+$. $[(CoL^1)^+] = 9.5 \times 10^{-5}$ M, [MeIm] = 0.25 M.

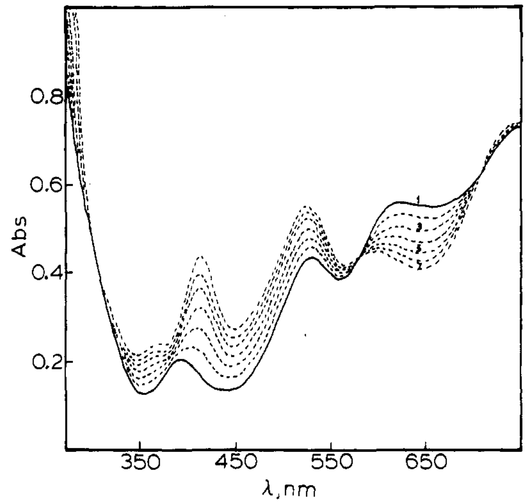

Figure 5. Electronic absorption spectra of $(CoL^1)^+$ during a titration with py, in acetonitrile with 0.1 M NBu_4ClO_4. $[CoL^1] = 1.15 \times 10^{-4}$ M and [py] = (1) 0, (2) 1.33×10^{-4} M, (3) 3.33×10^{-4} M, (4) 6.66×10^{-4} M, (5) 1.33×10^{-3} M, (6) 2.66×10^{-3} M, and (7) 1.9×10^{-2} M.

Thermodynamics of $Co^IL(B)^+$ Adduct Formation (B = py, MeIm, lut, Br^-). Addition of a slight stoichiometric excess of B to an An solution of CoL^+ results in rapid axial ligation to produce an adduct containing 1 molecule of B/Co (vide infra), according to (1). The electronic spectrum of the adduct of $(CoL^1)^+$ with MeIm is shown in Figure 4. Adducts of the other complexes with B exhibit similar spectra. Absorption maxima and extinction coefficients are collected in Table I.

A spectrophotometric titration was performed for each complex, CoL^+, with each Lewis base, B. The titration of $(CoL^1)^+$ with py is shown in Figure 5. The existence of isosbestic points at 706, 579, and 309 nm is strong evidence in support of the 1:1 stoichiometry indicated in (1). A plot of the left side of (2) at λ = 650 nm versus ln [py], where [py] is the concentration of free py in solution, is shown in Figure 6. The slope of the plot is 1.01, confirming 1:1 stoichiometry, and the intercept gives $K_{eq} = 2.3 \times 10^3$ M^{-1}. Titrations for the remaining systems confirm 1:1 stoichiometry and give the K_{eq} values collected in Table III. (In some cases, isosbestic points were not perfectly crisp, due to leakage of very small amounts of O_2 into the spectrophotometer cell during addition of B. However, deviations were small and in a manner consistent with reaction of Co^IL with O_2.[43] In all cases, data for plots like that in Figure 6 were obtained by measuring the absorbance at fixed wavelength in the glovebox. In this way,

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(45) Gillard, R. D.; Vaughan, D. H. *Transition Met. Chem. (Weinheim, Ger.)* **1978**, 3,44.

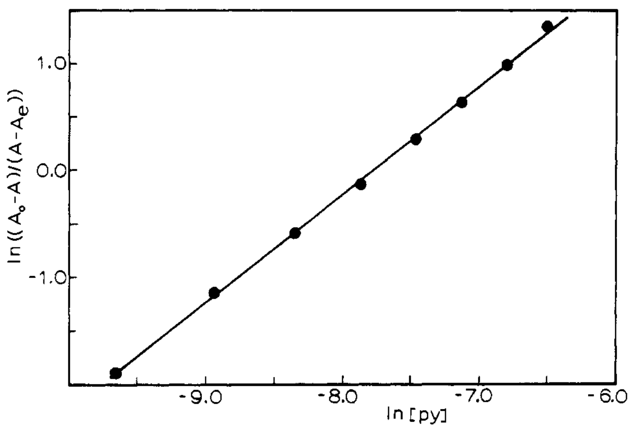

Figure 6. Plot of ln $((A_0-A)/(A-A_e))$ vs. ln [py] for reaction (1). Concentrations are similar to those indicated in Figure 5.

Table III. Equilibrium Constants for CoL^+–B Adduct Formation

system	q	$10^{-3}K_{eq}$, M^{-1}
$(CoL^1)^+$–MeIM	1.0	11 ± 3
$(CoL^1)^+$–py	1.0	2.3 ± 0.4
$(CoL^1)^+$–Br^-	1.0	0.23 ± 0.04
$(CoL^2)^+$–MeIm	0.98	33 ± 3
$(CoL^2)^+$–py	1.04	5.7 ± 0.3
$(CoL^2)^+$–lut	1.10	0.046 ± 0.002
$(CoL^5)^+$–MeIm	1.10	127 ± 5
$(CoL^5)^+$–py	1.01	4.5 ± 0.1
$(CoL^5)^+$–Br^-	1.04	1.8 ± 0.2
$(CoL^5)^+$–lut	1.22	0.089 ± 0.004

problems with oxygen were avoided.)

The equilibrium constants, K_{eq}, increase in the order lut < Br^- < py < MeIm for a given macrocyclic ligand L. This ordering is as expected based on the donor strengths of these species. For a given B, for example MeIm, the values increase in the order $L^1 < L^2 < L^5$. This ordering is understandable in terms of the withdrawing ability of the macrocyclic ligand substitutents. L^5, with phenyl groups on the imine carbons, should withdraw electron density from Co^I more effectively than should L^1, which has methyl substituents. The metal ion is therefore more acidic in $(CoL^5)^+$ than in $(CoL^1)^+$. The question remains, however, as to why the complexes are acidic at all. They are in fact potent Lewis acids, binding a variety of bases with equilibrium constants which are in all cases >50 M^{-1}. Electrochemical results show that the Co^I complexes are much more acidic than the corresponding Co^{II} complexes. This is unexpected, the higher charge of Co(II) normally making it a stronger acid. Further, preliminary experiments indicate that although the complex $(Ni^{II}L)^{2+}$ binds pyridine in the axial sites quite strongly, it is a weaker Lewis acid than $(Co^IL^1)^+$.[46] In this case, where the metals have the same configuration, it is truly remarkable that the stronger acid is the complex with smaller positive charge.

The relative acidities of CoL^+ and CoL^{2+} described above may be tentatively explained in at least two ways. The first explanation attributes the acidity of CoL^+ to the ability of the α-diimine macrocyclic ligands to function as a π-acceptors. Matchups of the metal d π donor orbitals with the π^* orbitals of the macrocycle is much better for Co^I than for Co^{II}, leading to extensive backbonding in CoL^+. It is conceivable that backbonding is so effective that the cobalt center may actually be *more positive* in CoL^+ than in CoL^{2+}. According to this explanation, CoL^+ should be a stronger acid than CoL^{2+} toward any Lewis base, regardless of the base characteristics.

A reviewer has suggested a second explanation based on the relative electrostatic and covalent characters of CoL^+ and CoL^{2+}. According to this explanation, CoL^{2+} is a primarily electrostatic acid and prefers electrostatic donors such as acetonitrile (with a large Drago E number[47]) to more covalent donors such as Py and MeIm (large Drago C number). Thus displacement of An solvent from the axial sites of CoL^{2+} is unfavorable. In contrast, CoL^+ is a primarily covalent acid and prefers covalent donors to electrostatic ones. Thus displacement of An solvent from the axial sites of CoL^+ is favorable. Experiments to differentiate between these two explanations are under way.

Registry No. $[CoL^1(An)_2](ClO_4)_3$, 63122-92-9; $[CoL^2(An)_2](ClO_4)_3$, 103093-30-7; $[CoL^5(An)_2](ClO_4)_3$, 103093-28-3; $CoL^1(An)_2(BPh_4)_2$, 73871-70-2; $CoL^2(An)_2(BPh_4)_2$, 111140-32-0; $CoL^5(An)_2(BPh_4)_2$, 111140-34-2; $[CoL^1](BPh_4)$, 111140-36-4; $[CoL^2](BPh_4)$, 111140-38-6; $[CoL^5](BPh_4)$, 111140-40-0; py, 110-86-1; MeIm, 616-47-7; Int, 108-48-5; DTBP, 585-48-8.

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Iowa State University, Ames, Iowa 50011

Molecular Orbital Study of Coenzyme B_{12}. Activation of the Cobalt–Carbon Bond by Angular Distortions

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A realistic model for coenzymes B_{12}, and the first one to contain the actual corrin and imidazole ligands, $Co(corrin)Im(CH_3)^+$, is examined with nonparametrized, iterative molecular orbital calculations by the Fenske–Hall method. Possible effects of the following four structural deformations on the Co–C bond strength are considered: tilt, θ, of the Co–C bond with respect to the corrin ring; distortion, ϕ, of configuration at the C atom; variation, d, of the Co–Im distance trans to the organic ligand; and rotation, ω, of the imidazole ligand. The first two deformations labilize the Co–C bond greatly; the third has a minor effect on its strength; and the fourth has no direct effect. The tilt of the organic ligand and the unusual configuration of the C atom, prominent structural features of coenzymes B_{12}, seem to be significant for their catalytic function. The theoretical findings contradict the notion that an agostic interaction exists between a C–H bond and the Co atom in B_{12} and corroborate the notion that the organic radical may perhaps be trapped by weak, reversible binding to the corrin macrocycle.

Introduction

Coenzyme B_{12} or 5′-deoxyadenosylcobalamin, designated AdB_{12}, together with some dozen enzymes catalyzes rearrangement reactions of various substrates. Methylcobalamin, designated MeB_{12}, with its enzymes catalyzes methylation reactions. The first organometallic compounds with a biological function, these and other cobalamins have been subjects of much research.[1-15] It is accepted

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(1) Dolphin, D., Ed. *B_{12}*; Wiley-Interscience: New York, 1982; 2 vols.

(2) Halpern, J. *Science (Washington, D.C.)* **1985**, *227*, 869.

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