

The Photochemistry of Organocobalt Complexes Containing Tetraaza Macrocyclic Ligands. Cobalt–Methyl Homolysis and the Nature of the Cobalt–Carbon Bond¹

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Abstract: Irradiations of $\text{Co}([\text{14}] \text{aneN}_4)(\text{OH}_2)\text{CH}_3^{2+}$ and $\text{Co}([\text{14}] \text{tetraeneN}_4)(\text{OH}_2)\text{CH}_3^{2+}$ result in $\text{Co}-\text{CH}_3$ homolysis. The quantum yields for homolysis are large and wavelength independent for the $[\text{14}] \text{aneN}_4$ complex and vary by only a factor of 2 for the $[\text{14}] \text{tetraeneN}_4$ complex for excitations with $254 \text{ nm} \leq \lambda \leq 540 \text{ nm}$. The homolysis threshold energies are small, $E_{\text{th}} = 1.6 \mu\text{m}^{-1}$ for $\text{Co}([\text{14}] \text{tetraeneN}_4)(\text{OH}_2)\text{CH}_3^{2+}$ and $E_{\text{th}} \leq 1.8 \mu\text{m}^{-1}$ for $\text{Co}([\text{14}] \text{aneN}_4)(\text{OH}_2)\text{CH}_3^{2+}$. The radical fragments recombine very efficiently and the reactions of $\text{Co}^{\text{II}}([\text{14}] \text{tetraeneN}_4)$ with the methyl and peroxymethyl radicals have been investigated by means of flash photolysis. A correlation of the energy levels of the $\text{Co}^{\text{II}}(\text{N}_4)$ and $\text{Co}(\text{N}_4)(\text{OH}_2)\text{CH}_3^{2+}$ complexes permits assignment of electronic transitions in $\text{Co}([\text{14}] \text{aneN}_4)(\text{OH}_2)\text{CH}_3^{2+}$. The assignment of transitions in $\text{Co}([\text{14}] \text{tetraeneN}_4)(\text{OH}_2)\text{CH}_3^{2+}$ remains more ambiguous. However, in neither case can the photohomolysis be associated with a low energy charge transfer absorption band. An orbital energy level scheme is proposed which accommodates the weak $\text{Co}-\text{CH}_3$ bond and most of the spectroscopic properties.

Since the discovery of coenzyme-B₁₂ and the related alkyl cobalamins,^{2,3} there has been a great deal of interest in the nature of the cobalt-carbon bond. Among the reactions characteristic of the cobalt-alkyl bond, the photochemical reactions have been found to be efficient, often straightforward,⁴⁻⁸ with the absorption of visible light leading to homolytic rupture of the $\text{Co}-\text{C}$ bond to form an alkyl radical and a cobalt(II) complex. The minimum energy required for photochemical homolysis, E_{th} , of a transition metal-ligand bond is a quasi-thermodynamic quantity which can be related to the metal-ligand bond energy.⁹ It is thus of interest that cobalt-alkyl homolyses have often been reported to occur for lower energy irradiations³⁻⁸ than most cobalt-halide homolyses,^{9,10} since this implies that the cobalt-alkyl bonds are relatively weak.

Unfortunately the inference of relatively weak cobalt-alkyl bonding is complicated by recent claims that low energy excitations of alkyl-cobalt bis(dimethylglyoximate)s in non-aqueous solvents lead to the production of hydrogen atoms and cobalt(II),⁸ and that photohomolysis of methylcobalamin is not important in the absence of oxygen.^{4b} In fact there have been relatively few thorough photochemical studies of alkyl cobalt systems, the work of Taylor et al.⁷ being an important exception.

We have chosen to investigate the photochemistry of two complexes containing synthetic macrocyclic ligands,

$\text{Co}([\text{14}] \text{tetraeneN}_4)(\text{OH}_2)\text{CH}_3^{2+}$ ¹¹ and $\text{Co}([\text{14}] \text{aneN}_4)(\text{OH}_2)\text{CH}_3^{2+}$, with a view of further investigating the nature of the cobalt-alkyl bond. These relatively new systems^{12,13} were selected for this study owing to differences in their unsaturation, contrasts in their absorption spectra,¹³ and their very similar stereochemistry.¹⁴ The visible-ultraviolet absorption spectrum of $\text{Co}([\text{14}] \text{tetraeneN}_4)(\text{OH}_2)\text{CH}_3^{2+}$ is more complex and the absorption bands are more intense than one finds for $\text{Co}^{\text{III}}([\text{14}] \text{tetraeneN}_4)\text{X}_2$ ($\text{X} = \text{H}_2\text{O}, \text{NH}_3, \text{Cl}, \text{CN}, \text{Br}, \text{NCS}, \text{etc.}$) complexes. In contrast, $\text{Co}([\text{14}] \text{aneN}_4)(\text{OH}_2)\text{CH}_3^{2+}$ exhibits a "typical" cobalt(III) spectrum with weak ($\epsilon \approx 10^2$) transitions observed at 478 and 370 nm. A simple "ligand field" interpretation of the lowest energy spin allowed transition ($\lambda_{\text{max}} 478 \text{ nm}$) of $\text{Co}([\text{14}] \text{aneN}_4)(\text{OH}_2)\text{CH}_3^{2+}$ would require relatively large ligand field stabilization energy (comparable to that of $\text{Co}(\text{NH}_3)_6^{3+}$) and, consequently, a relatively large energy for homolysis.⁹

Photohomolyses of cobalt-alkyl complexes have very often been described in terms of mechanisms involving population of $\text{Co}-\text{C}$ charge transfer excited states.^{5,8} However, the organocobalt complexes containing saturated equatorial ligands do not exhibit low-energy charge transfer bands. Consequently the investigation of low-energy homolytic processes in these systems should bear on this mechanistic argument as well as provide new insight into the nature of bonding in these complexes.

Experimental Section

1. Preparation of Materials. (a) **1,4,8,11-Tetraazacyclotetradecane** ($[\text{14}] \text{aneN}_4$). The compound was prepared according to the procedure of Barefield and Wagner.¹⁵ The purified product was light brown, mp 186.5–187.5 °C.

(b) $[\text{Co}([\text{14}] \text{aneN}_4)\text{CoCl}_4]$.¹⁶ A sample of 2.6 g of anhydrous CoCl_2 was slowly added to 2 g of $[\text{14}] \text{aneN}_4$ in 25 mL of DMF under a nitrogen atmosphere. The mixture was heated to 70 °C and stirred for 1 h. After cooling to room temperature, the precipitate was suction filtered and washed with several portions of a deaerated methanol-ether mixture (1:3 v/v). The product, green in color, was stored under nitrogen, yield 4 g.

(c) $[\text{Co}([\text{14}] \text{aneN}_4)(\text{OH}_2)\text{CH}_3(\text{Cl})_4]_2$.^{16,17} To 4 g of methylhydrazine in 200 mL of water in a beaker was added 4 g of $[\text{Co}([\text{14}] \text{aneN}_4)]\text{CoCl}_4$. The mixture was stirred at 50 °C to reduce the volume to 100 mL. After cooling, the mixture was filtered. Concentrated HClO_4 was added to the filtrate until the pH value reached about unity, whereupon the brown precipitate appeared. The precipitate was dissolved in 140 mL of water and AgClO_4 was added to the solution. After fil-

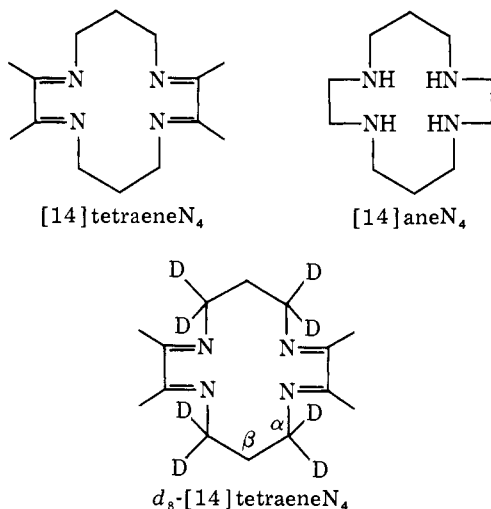


Table I. Molar Absorptivities and Absorption Maxima^a

[Co(tetraeneN ₄)(OH ₂)CH ₃](ClO ₄) ₂	ε(254) 3120	ε _{max} (421) 1600	ε _{max} (485) 2660	ε(542) 124	
[Co(tetraeneN ₄)(OH ₂) ₂](ClO ₄) ₂	ε(421) 524	ε(485) 1390	ε _{max} (542) 3100		
[Co([14]aneN ₄)(OH ₂)CH ₃](ClO ₄) ₂	ε _{max} (205) 23 800	ε(254) 1610	ε _{max} (370) 103	ε(420) 24	ε _{max} (478) 82
<i>trans</i> -[H ₂ O([14]aneN ₄)CoO ₂ Co([14]aneN ₄)-OH ₂](ClO ₄) ₄	ε(370) 1500	ε(420) 443	ε(478) 316		
[Co([14]aneN ₄)(OH ₂) ₂](ClO ₄) ₂	ε _{max} (337) 34	ε(370) 23	ε _{max} (470) 33	ε(478) 32	

^a Solvent was 1.0 × 10⁻³ M HClO₄, except for [Co([14]aneN₄)(OH₂)₂](ClO₄)₂, which was in 0.1 M HClO₄. Wavelengths in nm are indicated in parentheses. Listings are for wavelengths used in calculations of the concentrations of various species in photolyte solutions.

tration the volume of solution was reduced to 50 mL through heating at 85 °C. The solution was cooled and mixed with concentrated HClO₄. The resulting brown crystals were filtered, washed with a small amount of water, and air dried, yield 0.8 g.

Anal. Calcd for CoC₁₁H₂₉N₄O₉Cl₂: C, 26.90; H, 5.95; N, 11.41; Cl, 14.43. Found: C, 26.29; H, 6.29; N, 11.12; Cl, 14.10.

(d) *trans*-[Co([14]tetraeneN₄)Cl₂]. The compound was prepared according to the method of Farmery and Busch.¹⁸

(e) *trans*-[Co([14]tetraeneN₄)(OH₂)₂ClO₄]. We added 17 mL of 2.4 M AgClO₄ to a suspension of 5 g of [Co([14]tetraeneN₄)Cl₂]Cl in 117 mL of 0.1 N HClO₄. The white precipitate of AgCl was removed by filtration after heating. The filtrate was evaporated to a volume of 15 mL, filtered, and cooled. The dark brown crystals were suction filtered, washed with small portions of ethyl alcohol, and air dried. The yield was 5.3 g.

(f) [Co([14]tetraeneN₄)(OH₂)CH₃](ClO₄)₂.^{12,16,18} A solution of 8.3 mmol (5.3 g) of [Co([14]tetraeneN₄)(OH₂)₃](ClO₄)₃ in 300 mL of methanol-acetone mixed solvent (1:6.5 v/v) was bubbled with nitrogen for 50 min. Under vigorous stirring 16.5 mmol of NaBH₄ (0.630 g) was added; after 5 s excess CH₃I (60 mL) was introduced, and the mixture was suction filtered. The volume of the solution was reduced to 40 mL with a rotary evaporator. The resulting precipitate was filtered and dried, and recrystallized twice from aqueous HClO₄ solution. The final crystals were orange in color, yield 1.4 g.

Anal. Calcd for CoC₁₄H₂₉N₄O₉Cl₂: C, 33.41; H, 5.42; N, 10.39; Cl, 13.15. Found: C, 33.91; H, 5.67; N, 10.59; Cl, 12.84.

(g) [Co(*dg*-[14]tetraeneN₄)(OH₂)CH₃](ClO₄)₂. This compound was prepared using [Co(*dg*-[14]tetraeneN₄)(OH₂)₂](ClO₄)₂¹⁹ as starting material. The procedure was the same as that described in the preceding section, except for a 50% reduction in the stoichiometric amount of NaBH₄.

(h) *trans*-[H₂OCo([14]aneN₄)O₂([14]aneN₄)Co(OH₂)](ClO₄)₄. The compound was prepared according to a method reported in the literature.²⁰

2. Equipment. For photolysis at 254 nm, a low-pressure Hg lamp was used. For quantum yield measurements the light was collimated through a lens, and passed through a 1-cm filter solution of 2,7-dimethyl-3,6-diazacyclohepta-1,6-diene perchlorate in water (0.022%) before reaching the photolysis cell.

For irradiation at wavelengths other than 254 nm a 2000-W Hanovia Xe compact arc lamp, type L5239-100, was employed in conjunction with a collimating lens, a Bausch and Lomb grating monochromator, and glass filters (Table X1).²¹

Spectroscopic measurements were performed with a Cary 14 spectrophotometer. Spectral parameters of the complexes used are given in Table I.

Gaseous products were analyzed with an AEI mass spectrometer, Model MS 902, and a Hewlett-Packard F & M 720 gas chromatograph. Argon carrier gas was used with a 6-ft column of molecular sieve 5A, 45-60 mesh, in the chromatographic determinations.

The Xenon Corp., Watertown, Mass., Model 720 flash photolysis apparatus was employed.

NMR spectra were determined on a Varian T60 and IR spectra were taken on a Perkin-Elmer Model 621 spectrometer.

Cyclic voltammetry in acetonitrile was performed with a Chemtrix SSP-2 using an external voltmeter for improved accuracy and a standard calomel reference cell.^{22,23}

3. Photolysis Procedures. (a) [Co([14]tetraeneN₄)(OH₂)CH₃](ClO₄)₂. (i) In most cases, photolysis was performed with deaerated solutions.

(ii) Photolyses were also performed using aerated solutions.

(iii) For determinations of the relative yield of gaseous products, solutions were degassed prior to photolysis. Different photolysis ap-

paratuses were used for the mass spectrometric and chromatographic determinations; the former required photolysis of about 8 mL of solution, the latter about 48 mL. Solutions to be degassed were first purged with N₂, then four freeze-pump-thaw cycles before transfer to a quartz cell fused to the apparatus. Gaseous products were transferred to a collecting vessel or a gas loop on the vacuum line by means of a Toepler pump.

(iv) Experiments were carried out in which the Co^{II}(N₄') (N₄' represents the macrocyclic ligand which may or may not be totally intact after photolysis, *vide infra*) produced during photolysis was isolated and converted into solid Co^{III}(N₄')Cl₂ in order to obtain the infrared spectrum. About 19 mL of solution was introduced into a (10 × 1.9 cm) cylindrical quartz cell and purged with Cr²⁺ scrubbed nitrogen for 1 h. The N₂ purge was continued during irradiation. After irradiation the volume of solution was reduced to 6 mL. The solution was filtered, mixed with 4 mL of concentrated HCl, evaporated to 2 mL, and finally mixed with 1.5 mL of a 3 M solution of NaClO₄. After cooling the green precipitate was collected through suction filtration, washed with water, and air dried.

(b) [Co([14]aneN₄)(OH₂)CH₃](ClO₄)₂. Most photolyses were performed on deaerated solutions. The extent of photoredox reaction was determined from absorbance changes in the photolyte and from the yield of μ -peroxy complex, following oxidation, to monitor the production of Co^{II}([14]aneN₄). To introduce oxygen, the serum cap on the photolysis cell was removed after irradiation, and oxygen was bubbled through the solution for 2 min. Absorbance changes were measured at 420 nm. Concentrations of Co^{II}([14]aneN₄) so determined were in good agreement with absorbance changes in the photolyte using data from Table I.

(c) **Actinometry.** The potassium ferrioxalate actinometer²⁴ was used for light of wavelength equal to or shorter than 370 nm, and the Reinecke actinometer²⁵ was used at longer wavelengths.

Results

A. General. Electrochemical reductions of the cationic Co(N₄)(OH₂)CH₃²⁺ complexes were observed only at very negative potentials. In acetonitrile (AN) solutions two cathodic waves were observed for Co([14]aneN₄)(AN)CH₃²⁺: $E_{1/2} = -0.78$ and -1.29 V (vs. SCE; waves were respectively irreversible and reversible). Under similar conditions we observed three cathodic waves for Co([14]tetraeneN₄)(AN)CH₃²⁺: $E_{1/2} = -0.79$, ~ -1.2 , and -1.34 V (vs. SCE; all waves irreversible). No anodic waves were observed for either cationic complex for $E < +1.4$ V. No cathodic wave was observed for Co(DMG)₂(py)Me for $E > -2$ V, and the quasi-reversible anodic wave was observed at $E_{1/2} = +0.75$ V.

Acidic solutions of Co([14]tetraeneN₄)(OH₂)CH₃²⁺ or of Co([14]aneN₄)(OH₂)CH₃²⁺ exhibited no signs of decomposition when stored in the dark for periods of at least a day. However, exposure of solutions of either complex to laboratory light for comparable periods resulted in extensive decomposition, as manifested by absorbance changes in the visible region. We have systematically examined the photochemistry of both complexes as described below.

B. [Co([14]tetraeneN₄)(OH₂)CH₃](ClO₄)₂. Photolysis was carried out at various incident wavelengths, both in deaerated and air-saturated solutions. In all cases solutions contained 1.0 × 10⁻³ M HClO₄.

1. Photolysis in Deaerated Solutions. During photolysis the initially orange solution became red. Spectral changes during irradiation were recorded (Figure 1) and the same isosbestic

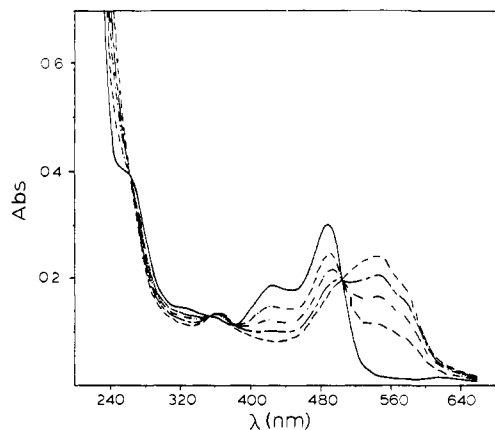


Figure 1. Spectral changes during photolysis of $[\text{Co}(\text{[14]tetraeneN}_4)(\text{OH}_2)\text{CH}_3](\text{ClO}_4)_2$ in deaerated solution. $[\text{Complex}]_0 = 1.13 \times 10^{-4} \text{ M}$; $[\text{HClO}_4] = 1.0 \times 10^{-3} \text{ M}$; λ 254 nm. Irradiation time: —, 0; - - - -, 20 min; ·····, 51 min; - · - ·, 101 min; - - - -, 210 min.

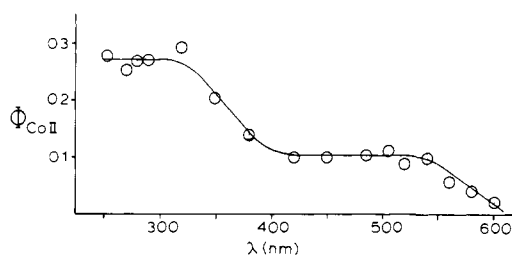


Figure 2. Photolysis of $[\text{Co}(\text{[14]tetraeneN}_4)(\text{OH}_2)\text{CH}_3](\text{ClO}_4)_2$. Effects of changing incident wavelength. Points are averages of several determinations. Errors in replicate determinations average less than or equal to 10% for $\lambda < 380 \text{ nm}$; less than or equal to 20% for $380 \text{ nm} \leq \lambda < 485 \text{ nm}$; and less than or equal to 30% for $\lambda \geq 485 \text{ nm}$ (see Table S2).

points were observed for irradiations at 254, 420, and 485 nm. The spectral features and isosbestic points are characteristic of the formation of the $\text{Co}^{\text{II}}(\text{[14]tetraeneN}_4)$ species.

The concentration of $\text{Co}^{\text{II}}(\text{N}_4)$ formed was calculated from the changing absorbance values and extinction coefficients of $[\text{Co}(\text{[14]tetraeneN}_4)(\text{OH}_2)\text{CH}_3](\text{ClO}_4)_2$ and $[\text{Co}(\text{[14]tetraeneN}_4)(\text{OH}_2)_2](\text{ClO}_4)_2$ at 542 and 484 nm (or 421 nm), with corrections made for a small amount of $\text{Co}^{\text{III}}(\text{N}_4)$ produced due to oxidation by residual oxygen in the photolyte. A plot of $[\text{Co}^{\text{II}}(\text{N}_4)]$ produced due to oxidation by residual oxygen in the photolyte. A plot of $[\text{Co}^{\text{II}}(\text{N}_4)]$ as a function of irradiation time [Figure S1²¹] indicates that the rate of formation of $\text{Co}^{\text{II}}(\text{N}_4)$ decreases with time. Quantum yields were calculated by dividing the initial rate with the rate of light absorption and the values at different wavelengths are listed in Table X2²¹ and Figure 2

2. Photolysis in Aerated Solution. When the complex concentration was low ($\sim 10^{-4} \text{ M}$), photolyses in a 1-cm cell in the presence of air did not give rise to noticeable solution color change. Spectra variations as a function of irradiation time are shown in Figure 3. The final product was not $\text{Co}^{\text{II}}(\text{[14]tetraeneN}_4)$ or $\text{Co}(\text{[14]tetraeneN}_4)(\text{OH}_2)_2^{3+}$.

For short irradiation periods there was no detectable increase of absorbance at 542 nm; however, there was a linear decrease of absorbance at 485 nm from which one can estimate the amount of product formed as a function of time. This rate of $\text{Co}^{\text{II}}(\text{N}_4)$ formation can be used to calculate the quantum yield for the homolysis reaction. Linear plots of $\text{Co}^{\text{II}}(\text{N}_4)$ vs. time were always obtained for short-term irradiations (e.g., Figure S2). Quantum yield values obtained in this way were comparable to those obtained in deaerated solutions (Table S2²¹).

3. Photoproducts. (a) Gaseous Product Analysis. Methane and ethane were detected in mass spectrometric analysis and

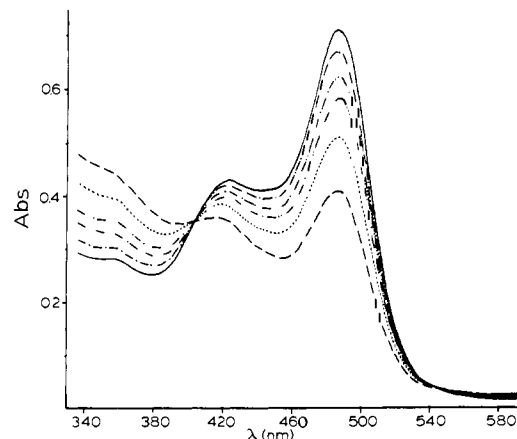


Figure 3. Spectral change during photolysis of $[\text{Co}(\text{[14]tetraeneN}_4)(\text{OH}_2)\text{CH}_3](\text{ClO}_4)_2$ in aerated solution. λ 254 nm; $[\text{HClO}_4] = 1.0 \times 10^{-3} \text{ M}$. Irradiation time: —, 0; - - - -, 1 min; ·····, 2.5 min; - · - ·, 4 min; ·····, 7 min; - - - -, 12 min.

the results are summarized in Table II. We were unable to use mass spectrometry to set limits on hydrogen evolution owing to irreproducible sensitivity toward hydrogen, and because hydrogen appeared to be a fragmentation product of a mixture of methane and ethane. It was found that hydrogen could be conveniently analyzed gas chromatographically if argon was used as the carrier gas; the relative response (peak area/mol) of the detector toward the three gases was $\text{H}_2:\text{CH}_4:\text{C}_2\text{H}_6 = 3.91:1.13:1.00$ (Table II). Analysis of photolyzed samples showed no detectable hydrogen.

(b) Coordination Complex Products. Irradiations of this complex in deaerated solution always resulted in the characteristic 542-nm absorption of $\text{Co}^{\text{II}}(\text{N}_4)$ species. Photolyses of aerated solutions yielded a cobalt(III) product other than $\text{Co}(\text{[14]tetraeneN}_4)(\text{OH}_2)_2^{3+}$. In addition to the spectroscopic observations, we have used other means to characterize these products.

(i) NMR spectra demonstrated that the cobalt(III) product of photolysis in aerated solutions had a single methyl resonance

Table II. Photolysis of $[\text{Co}(\text{[14]tetraeneN}_4)(\text{OH}_2)\text{CH}_3](\text{ClO}_4)_2$. Relative Yields of Methane and Ethane

Run ^a	$[\text{Complex}]_0^b$ $\times 10^3, \text{ M}$	% reaction	Methane:ethane	$\text{CH}_4:\text{CH}_3\text{D}$
1	5.52	44	1.0:1.5	
2	5.77	44	1.0:1.6	^c
3 ^d	4.89	38	1.0:1.6	1.0:1.0
4 ^e	5.13	44	1.0:0.05	1.0:0.03
5 ^f	3.40	37	1.0:1.5	
6 ^f	3.61	45	1.0:1.4	

^a Gases were analyzed with a mass spectrometer for runs 1–4, and with a gas chromatograph for runs 5 and 6. Incident wavelength was 254 nm for the first five runs; it was $>450 \text{ nm}$ (light passing through collimating lens and filter 3-72; see Table S1²¹) for the last run. ^b Initial concentration of $[\text{Co}(\text{[14]tetraeneN}_4)(\text{OH}_2)\text{CH}_3](\text{ClO}_4)_2$. Solvent was $1.0 \times 10^{-3} \text{ M HClO}_4$, except for run 2, for which solvent was $1.0 \times 10^{-3} \text{ M DClO}_4$ in D_2O . ^c There was a very small peak at mass/charge ratio 17; the height was about that expected for natural abundance of ^{13}C , judging from calibration using methane. ^d Complex was $[\text{Co}(d_8\text{-[14]tetraeneN}_4)(\text{OH}_2)\text{CH}_3](\text{ClO}_4)_2$. ^e $[\text{Co}(d_8\text{-[14]tetraeneN}_4)(\text{OH}_2)\text{CH}_3](\text{ClO}_4)_2$ in the presence of 2.5 M isopropyl alcohol. ^f Argon was used as carrier gas, flow rate was 10 mL/28 s. At the column temperature of 37 °C, the retention time for hydrogen was 2.5 min (it was 9 min for methane); after the methane peak had emerged the column temperature was set to 80 °C, and the retention time of C_2H_6 was about 26 min from the time of temperature adjustment. In the product analysis no hydrogen was observed.

Table III. Flash Photolysis of $[\text{Co}(\text{[14]tetraeneN}_4)(\text{OH}_2)\text{CH}_3](\text{ClO}_4)_2$

Set-flash ^a	[Complex] ₀ ^b × 10 ⁵ , M	[Co ^{II} (N ₄) ₀] ^c × 10 ⁶ , M	[O ₂ CH ₃] ₀ ^d × 10 ⁶ , M	Treatment of soln	k ₄ ^e × 10 ⁻⁸ , M ⁻¹ s ⁻¹
1-1	1.78	4.40	2.71	Aerated	1.1
1-2	1.78	4.50	2.77	Aerated	1.1
1-3	1.78	3.68	2.20	O ₂ saturated	1.4
2-1	1.11	6.98	4.35	Aerated	1.0
2-2	1.11	6.74	4.13	Aerated	1.2
2-3	1.11	6.60	4.20	O ₂ saturated	1.1
3-1	2.59	8.50	4.84	Aerated	1.3
4-1	1.98	8.02	4.10	Aerated	1.1
4-2	1.98	8.29	4.32	Aerated	1.2
4-3	1.98	8.61	4.85	O ₂ saturated	1.1
4-4	1.98	9.07	5.09	O ₂ saturated	1.1

^a Each set of experiments was carried out using a single substrate solution. Solutions were discarded after a single flash. In set 1, water was used to fill the cell jacket; in all other cases ethyl alcohol was used. ^b Initial concentration of $[\text{Co}(\text{[14]tetraeneN}_4)(\text{OH}_2)\text{CH}_3](\text{ClO}_4)_2$ in 1.0×10^{-3} M HClO₄. ^c Initial concentration of Co^{II}(N₄) produced immediately after flash, as calculated from absorbance at 542 nm before and after flash, and the voltage reading of the oscilloscope amplifier. ^d Initial concentration of that part of ·O₂CH₃ "available" for reaction 4, taken as $[\text{Co}^{\text{II}}(\text{N}_4)]_{t=0} - [\text{Co}^{\text{II}}(\text{N}_4)]_{t=\infty}$. ^e Average value of k₄ is $(1.19 \pm 0.12) \times 10^8$ M⁻¹ s⁻¹.

0.1 ppm upfield from the methyl resonance of Co([14]-tetraeneN₄)(OH₂)₂³⁺.

(ii) Two different photolyses were performed in deaerated solutions in which the cobalt(II) products were converted to Co(N₄)Cl₂⁺ for infrared analysis. For both runs the IR spectra of the [Co(N₄)Cl₂]ClO₄ samples were identical and they were similar to the spectrum of an authentic [Co([14]tetraene-N₄)Cl₂]ClO₄ sample except for an additional peak at 1644 cm⁻¹ and a weak absorption peak at 1167 cm⁻¹ in the product spectra (Table S4²¹).

4. Investigations of Radical Reactions. (a) Photolysis in the Presence of [Co(NH₃)₅O₂CCH₃](ClO₄)₂. The reaction between Co([14]tetraeneN₄)(OH₂)CH₃²⁺ and the methyl radical was investigated by irradiating a solution containing the cobalt alkyl complex and [Co(NH₃)₅O₂CCH₃](ClO₄)₂.²⁶ Less than 10% of the 254-nm radiation in these experiments was absorbed by Co([14]tetraeneN₄)(OH₂)CH₃²⁺. There was no enhancement of cobalt(II) yield attributable to ·CH₃ attack on the organocobalt substrate.

(b) Flash Photolysis. Flash photolyses were performed with deaerated, aerated, or oxygen-saturated solutions. For deaerated solutions, flash irradiations resulted in the immediate formation of Co^{II}(N₄), and no transient phenomena could be observed. For aerated and oxygen-saturated solutions, transient phenomena could be observed. Spectroscopic changes in the aerated solutions were suggestive of formation of the Co^{III}(N₄) product of continuous photolysis in aerated solutions. The ratio [Co^{II}(N₄):[Co^{III}(N₄)] could be estimated from absorbances of irradiated solutions and varied from 0.4 to 1 in different sets of experiments but was independent of whether the solution was aerated or saturated with O₂ and was insensitive to the wavelength region irradiated. Rate constants for the reaction of Co^{II}([14]tetraeneN₄) with the methyl peroxy radical are in Table III.

C. [Co([14]aneN₄)(OH₂)CH₃](ClO₄)₂. Owing to the smaller absorptivity we had to use about tenfold more concentrated solutions of this complex than were used for Co([14]tetraeneN₄)(OH₂)CH₃²⁺. Most photolyses were performed in 10⁻³ M HClO₄.

1. Photolyses in Deaerated Solutions. Irradiation with UV or visible light resulted in decrease of absorbance at 370 and 478 nm; however, there was a steady decline of the photolysis rate, and after a short initial period the reaction became too slow to follow conveniently. The reaction could be followed conveniently in aqueous 2-propanol solutions. Figure 4 illustrates the spectral changes during photolysis in the presence of the alcohol. Introduction of air or oxygen into the solution after photolysis resulted in very rapid oxidation of the co-

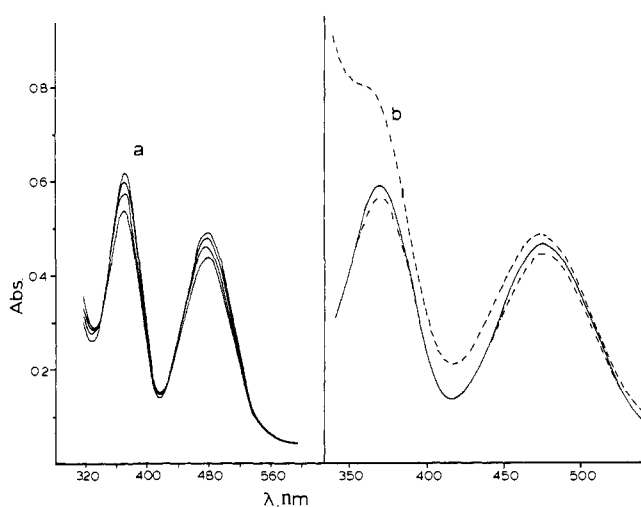


Figure 4. Photolysis of $[\text{Co}(\text{[14]aneN}_4)(\text{OH}_2)\text{CH}_3](\text{ClO}_4)_2$. $[\text{HClO}_4] = 1.0 \times 10^{-3}$ M; λ 254 nm. (a) $[\text{Complex}] = 5.94 \times 10^{-3}$ M; [isopropyl alcohol] = 1.60 M. Top curve = initial solution; second curve = 20 min irradiation; third curve = 56 min irradiation; bottom curve = 116 min irradiation. (b) $[\text{Complex}] = 5.69 \times 10^{-3}$ M; [isopropyl alcohol] = 2.00 M. —, initial solution; - - -, 44 min irradiation; - · - ·, after exposure to oxygen.

balt(II) product; e.g., see the upper curve in Figure 4b. The oxidation product proved to be unstable and its absorbance decreased slowly with time.

Comparison of spectra indicated that the oxidation product was the peroxo-bridged complex *trans*- $[\text{H}_2\text{OCo}(\text{[14]aneN}_4)\text{O}_2(\text{[14]aneN}_4)\text{CoOH}_2]^{4+}$. This μ -peroxo species is not stable in acidic solution.²⁰ In order to obtain extinction coefficients (Table I) of the dimeric species, absorbance values at various wavelengths were measured as a function of time and extrapolated to time zero. Several measurements were made for each of the extinction coefficients; those listed in Table I represent the largest values obtained, although the value at 420 nm fluctuated only slightly. Owing to its large absorptivity, the μ -peroxo complex provided a convenient basis for cobalt(II) analyses.

Quantum yields based on photolyses in deaerated aqueous 2-propanol solutions are collected in Table S2.^{21,27} These yields are averages of yields determined from decreases in substrate absorbance and from the yield of Co^{II}([14]aneN₄) as determined from oxidation to the μ -peroxo dimer.

3. Photolyses in Aerated Solution. The spectral changes are shown in Figure 5. Increase of acid concentration of 0.22 M

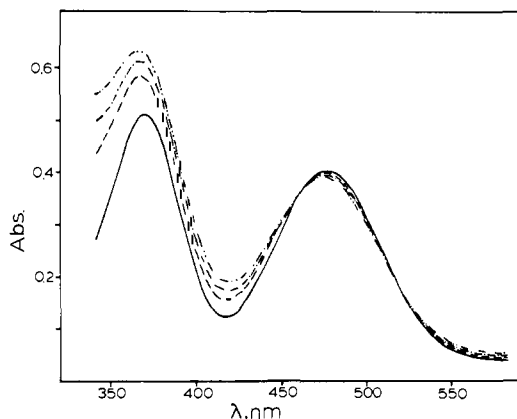


Figure 5. Photolysis of $[\text{Co}([\text{14}] \text{aneN}_4)(\text{OH}_2)\text{CH}_3](\text{ClO}_4)_2$ in aerated solution. λ 254 nm, $[\text{HClO}_4] = 1.0 \times 10^{-3}$ M. —, initial solution; - - -, 21 min irradiation; - · - ·, 38 min irradiation; · · ·, 64 min irradiation.

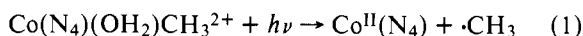
or addition of 2.0 M 2-propanol did not cause any noticeable difference in the changing pattern of the spectra.

4. Absorption Spectrum of $\text{Co}^{\text{II}}([\text{14}] \text{aneN}_4)$. A solution of known concentration was prepared by potentiometric titration of a solution of $[\text{Co}([\text{14}] \text{aneN}_4)(\text{OH}_2)_2](\text{ClO}_4)_3$ with chromous perchlorate under nitrogen atmosphere (the concentration of Cr^{2+} was determined by titration with a standard solution of ferric ammonium sulfate). Part of the solution at the end point of titration was transferred with syringe to a serum-capped cell which had been previously flushed with nitrogen. The spectrum, after correction for absorption due to Cr^{3+} , is shown in Figure 6. When the serum cap was removed to admit air to the system, the characteristic absorbance of the μ -peroxo complex was observed, as shown in the upper curve in Figure 6.

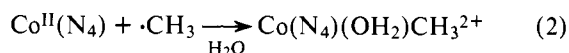
5. Dependence of Yields on 2-Propanol. Since quantitative determinations of yield were possible only in deaerated solutions containing 2-propanol, we have also investigated the effects of this alcohol on yields. The cobalt(II) yields reach a limiting value of about 0.3 for $[\text{2-propanol}] \approx 2$ M (Figure S3).

Discussion

A. Primary Photoprocesses. The only photoreaction observed at any wavelength for either $\text{Co}([\text{14}] \text{tetraeneN}_4)(\text{OH}_2)\text{CH}_3^{2+}$ or $\text{Co}([\text{14}] \text{aneN}_4)(\text{OH}_2)\text{CH}_3^{2+}$ is homolytic cleavage of the Co-CH₃ bond:



B. Secondary Thermal Reactions. The principal reaction complicating photochemical studies of the cobalt-alkyl complexes is the very efficient $\text{Co}^{\text{II}}(\text{N}_4)$ -alkyl recombination^{5c,6b,13,28}



for which $k_2 \sim 10^8 \text{ M}^{-1} \text{ s}^{-1}$. The effect of this reaction is a striking reduction of the photolysis rate as $[\text{Co}^{\text{II}}(\text{N}_4)]$ increases. This recombination reaction is effectively suppressed by various radical scavengers (e.g., 2-propanol or O_2).

Methane and ethane result from secondary reactions of the methyl radical. These gaseous species were also observed in the photolyses of methylcobalamin^{2,5b} and methylcobaloximes.^{5b} The source of ethane is undoubtedly the efficient methyl radical coupling reaction in aqueous solution (e.g., see ref 26). A significant proportion of the methane detected in the photolysis of $\text{Co}([\text{14}] \text{tetraeneN}_4)(\text{OH}_2)\text{CH}_3^{2+}$ must derive from a reaction of the methyl radical with the coordinated ligand. Furthermore, the results in Table II indicate that most

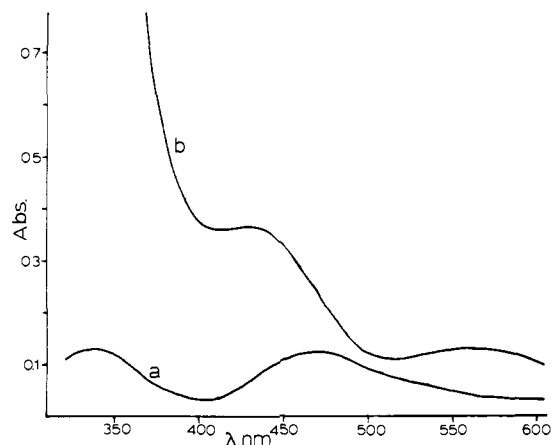
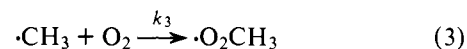


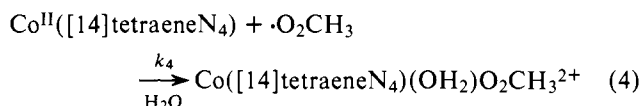
Figure 6. Spectrum of $[\text{Co}([\text{14}] \text{eneN}_4)(\text{OH}_2)_2](\text{ClO}_4)_2$. (a) $[\text{Complex}] = 4.42 \times 10^{-3}$ M. (b) After exposure to oxygen.

of the hydrogen atom abstraction occurs at an α carbon atom of the ligand. This apparently leads to formation of complexes involving a C=C bond between α and β carbon atoms of a six-membered chelate ring. While we are unable to determine if there is any difference in susceptibility to $\cdot\text{CH}_3$ attack of $\text{Co}^{\text{II}}(\text{N}_4)$ and $\text{Co}^{\text{III}}(\text{N}_4)$ complexes, if the methyl radical does attack the cobalt(III) substrate there is no detectable abstraction of the coordinated methyl group. Furthermore, since quantum yields obtained in the presence of 2-propanol or oxygen and initial quantum yields obtained in the absence of radical scavengers were found to be equal within experimental error, it is inferred that none of the radicals formed efficiently produce cobalt(II) species from the organocobalt substrates.

Although cobalt(II) complexes differ markedly in their reactivity toward oxygen, the reactions in the presence of oxygen seem reasonably straightforward. $\text{Co}^{\text{II}}([\text{14}] \text{tetraeneN}_4)$ can be kept in aerated acidic solutions for many hours with only slight decomposition while $\text{Co}^{\text{II}}([\text{14}] \text{aneN}_4)$ is oxidized completely to the μ -peroxo dimer within a few minutes. However, either system photolyzed in the presence of O_2 is efficiently converted into peroxocobalt(III) complexes. Owing to the much greater absorptivity of $\text{Co}([\text{14}] \text{tetraeneN}_4)(\text{OH}_2)\text{CH}_3^{2+}$ than the $\text{Co}^{\text{III}}([\text{14}] \text{tetraeneN}_4)\text{XY}$ complexes, oxygen was a very useful scavenger for use with this system. The flash photolysis data indicate that the dominant scavenging process in the presence of O_2 is the efficient ($k_3 \approx 4.7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$)²⁹ formation of the methylperoxy radical



followed by the rapid ($k_4 = (1.2 \pm 0.1) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$) reaction of this radical with $\text{Co}^{\text{II}}([\text{14}] \text{tetraeneN}_4)$.



While the evidence demonstrates that eq 2-4 describe the predominant thermal reactions of photochemically generated radical species, there are some additional reaction pathways which appear to make contributions to the overall distribution of reaction products. For example, a small amount of deuteriomethane appears to form from methyl radicals not scavenged by 2.5 M 2-propanol (run 4 of Table II) and this suggests a small contribution of a cage reaction. Furthermore, the cobalt(III):cobalt(II) ratios which result from continuous and flash photolyses in aerated solutions differ, and this suggests contributions of minor pathways in competition with eq 4 such as the peroxymethyl radical abstraction of a hydrogen atom

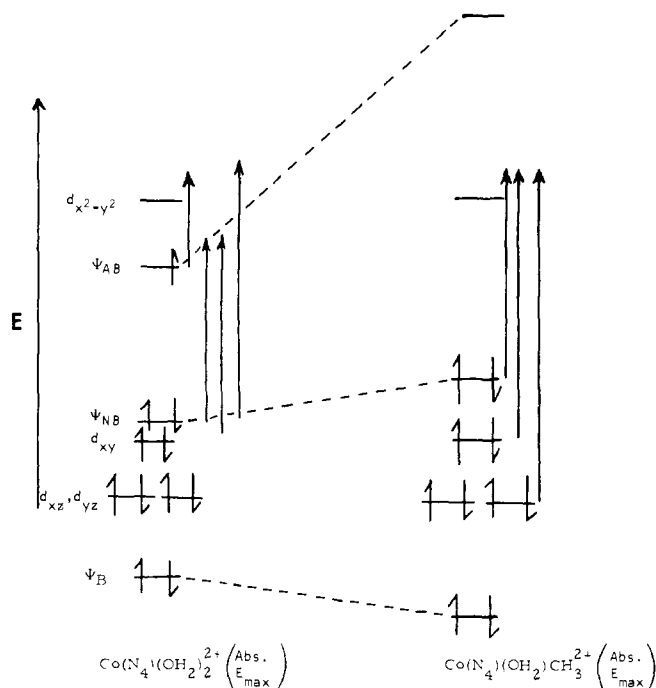


Figure 7. Proposed correlation of orbital energies and spectroscopic transitions in $\text{Co}([\text{14}] \text{aneN}_4)(\text{OH}_2)_2^{2+}$ and $\text{Co}([\text{14}] \text{aneN}_4)(\text{OH}_2)\text{CH}_3^{2+}$. The orbitals designated ψ_{AB} , ψ_{NB} , and ψ_B are the antibonding, nonbonding, and bonding orbitals of a three-center model for axial bonding interactions (ref 34); in the cobalt(II) complex the donor electrons of the axial ligand are considered to be largely ligand localized resulting in the symmetric splitting of orbitals in the three-center-five-electron axial bond. A similar three-center-four-electron model for the methyl complex would have a relatively high energy ψ_{AB} owing to the covalency of the $\text{Co}-\text{CH}_3$ bond. Vertical arrows indicate the relative energies of observed optical transitions. Although the relative energies of the orbitals are chosen to be consistent with spectroscopic and photochemical observations, the relative ordering of orbitals designated ψ_{NB} , d_{xy} , d_{xz} , and d_{yz} is ambiguous.

from the macrocyclic ligand and O_2 dehydrogenation of the intermediate ligand radical. Elucidation of these minor pathways will have to depend on studies different from those reported here.

C. Considerations of Energetics, Mechanism, and the Nature of the Cobalt-Carbon Bond. A very striking result of this study is the very low energy threshold for $\text{Co}-\text{CH}_3$ homolysis. For $\text{Co}([\text{14}] \text{tetraeneN}_4)(\text{OH}_2)\text{CH}_3^{2+}$ we estimate a threshold wavelength of 610 nm ($1.64 \mu\text{m}^{-1}$);³¹ for $\text{Co}([\text{14}] \text{aneN}_4)(\text{OH}_2)\text{CH}_3^{2+}$, the threshold excitation is $\lambda_0 < 540 \text{ nm}$ ($E_{\text{th}} < 1.85 \mu\text{m}^{-1}$). The minimum energy required for homolysis can be approximately partitioned into ionic (I), covalent (C), and ligand field (ΔLFSE) components:³¹ $E_{\text{th}} \approx I + C + \Delta\text{LFSE}$. For a cobalt-carbon bond one expects I to be small (the electronegativities of Co and CH_3 have been estimated to be 2.0³¹ and 2.3,³² respectively) and C should be reasonably large. Consequently a small threshold energy implies that ΔLFSE is small; e.g., smaller for $\text{Co}-\text{CH}_3$ than for cobalt-halide homolyses. Thus the low-energy homolysis threshold is in disagreement with the simple "ligand field" assignment of transitions mentioned in the introduction.

For acidopentaamminecobalt(III) complexes the homolysis threshold energies, E_{th} , average about $0.3 \mu\text{m}^{-1}$ less than the threshold energies for CTTM absorption, E'_{th} .⁹ Furthermore, values of E_{th} and E'_{th} can be estimated on the basis of various quasi-thermodynamic arguments.^{9,31} This suggests that the Coulomb integral is much larger than the exchange integral in MO expressions of the energy of the bonding and antibonding $\text{Co}-\text{X}$ orbitals (ψ_B and ψ_{AB} , respectively); thus for these complexes we have $E(\psi_{AB}) - E(\psi_B) \approx E_{\text{th}} \approx 2\beta$, where β is the average difference in energy between ψ_B and the partly

filled orbitals of $\text{Co}(\text{NH}_3)_5^{2+}$ and $\cdot\text{X}$.³³ In striking contrast the cobalt-methyl complexes must have $E(\psi_{AB}) - E(\psi_B) \gg E_{\text{th}}$, since the only strongly allowed transitions in $\text{Co}([\text{14}] \text{aneN}_4)(\text{OH}_2)\text{CH}_3^{2+}$ are deep in the ultraviolet. This suggests that the exchange integral makes a relatively large contribution to the orbital energies for the alkyl-cobalt complexes.³³

These several considerations permit us to construct a simple orbital correlation diagram for $\text{Co}([\text{14}] \text{aneN}_4)(\text{OH}_2)_2^{2+}$ and $\text{Co}([\text{14}] \text{aneN}_4)(\text{OH}_2)\text{CH}_3^{2+}$ (Figure 7). The absorption spectra of $\text{Co}([\text{14}] \text{aneN}_4)(\text{OH}_2)_2^{2+}$ (Figure 6) and the energy of the $\psi_{AB} \rightarrow d_{x^2-y^2}$ transition as inferred from EPR spectra³⁴⁻³⁶ permit us to make a reasonable assignment of orbital energies as indicated in Figure 7. The orbital energy level scheme proposed for $\text{Co}([\text{14}] \text{aneN}_4)(\text{OH}_2)_2^{2+}$ is based on a three-center-five-electron bonding model for the axial interactions.³⁴ If the same model is applied to $\text{Co}([\text{14}] \text{aneN}_4)(\text{OH}_2)\text{CH}_3^{2+}$, then one expects a stronger axial bonding interaction due largely to loss of electron density from ψ_{AB} .³⁷ Owing to the covalency of the $\text{Co}-\text{CH}_3$ bond, ψ_{AB} should occur at appreciably higher energy in the methyl complex than in the cobalt(II) complex. The relative orbital energies in Figure 7 have been selected to be consistent with the small threshold energy required for $\text{Co}-\text{CH}_3$ homolysis and with the energies of the observed electronic transitions (indicated by vertical arrows). The inferred $2\text{-}\mu\text{m}^{-1}$ difference in energy between the lowest unoccupied and the highest filled orbitals in $\text{Co}([\text{14}] \text{aneN}_4)(\text{OH}_2)\text{CH}_3^{2+}$ is consistent with the greater than 2.2 V ($1.8 \mu\text{m}^{-1}$) difference in half-wave potentials for oxidation and reduction of this complex.

The small molar absorptivities found for low energy optical transitions in $\text{Co}([\text{14}] \text{aneN}_4)(\text{OH}_2)_2^{2+}$ and $\text{Co}([\text{14}] \text{aneN}_4)(\text{OH}_2)\text{CH}_3^{2+}$ are consistent with a simple three center bonding model since only a symmetrical metal orbital is used in this approach. On the basis of the intensities of the observed transitions, a significant metal p-orbital contribution in ψ_B and ψ_{AB} can be ruled out in the cobalt(II) complex and does not seem to be required in the methyl complex. In contrast, the relatively intense low-energy transitions found for $\text{Co}([\text{14}] \text{tetraeneN}_4)(\text{OH}_2)\text{CH}_3^{2+}$ and other cobalt-alkyl complexes with unsaturated equatorial ligand systems suggest an antisymmetrical component in one of the orbitals involved. One possible interpretation of the transitions in these more complicated systems is that the low energy transition is largely charge transfer to ligand, (d_{xy} or ψ_{NB}) $\rightarrow \pi^*(\text{N}_4)$, with the energy of $\pi^*(\text{N}_4)$ being appreciably lowered due to configuration interaction with ψ_{AB} . This and related problems are being further investigated.

The relatively large value of the exchange integral inferred for the $\text{Co}-\text{CH}_3$ orbitals would give rise to a relatively low energy ($\psi_B \rightarrow \psi_{AB}$) triplet state. Such a state could well mediate the photochemistry. Alternatively the lowest energy excited state (probably $\psi_{NB} \rightarrow d_{x^2-y^2}$) could relax to populate the ground state in a reaction channel for homolytic dissociation.⁴⁰ Resolution of the mechanistic problem will have to await further information about these systems.

Acknowledgment. The authors are grateful to Professor H. B. Gray for a stimulating discussion of some of the questions raised in this manuscript.

Supplementary Material Available: Table S1 (glass filters used in photolysis), Tables S2a and S4 and Figure S1 (photolysis of $[\text{Co}([\text{14}] \text{tetraeneN}_4)(\text{OH}_2)\text{CH}_3](\text{ClO}_4)_2$), Table S2b and Figure S3 (photolysis of $[\text{Co}([\text{14}] \text{aneN}_4)(\text{OH}_2)\text{CH}_3](\text{ClO}_4)_2$), and Table S3 and Figure S2 (flash photolysis of $[\text{Co}([\text{14}] \text{tetraeneN}_4)(\text{OH}_2)\text{CH}_3](\text{ClO}_4)_2$) (8 pages). Ordering information is given on any current masthead page.

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- (1) (a) Partial support of this research by the National Institutes of Health (AM 14341) and the National Science Foundation (MPS 72 0509LA02) is gratefully acknowledged. (b) Additional support in the form of a fellowship and academic leave for C.Y.M. from Nanyang University, Singapore, is also gratefully acknowledged. (c) Preliminary reports of these studies have been made at the Vth IUPAC Symposium on Photochemistry, Aix-en-Provence, France, July 1976 (paper no. 26, p 79), and the 172nd National Meeting of the American Chemical Society, San Francisco, Calif., Aug 1976, Abstracts, No. INOR-8.
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Mechanism of Hydrogen Evolution from Hydridocobaloxime

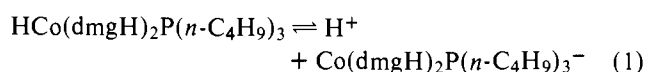
Tai-Hsiang Chao and James H. Espenson*

Contribution from the Ames Laboratory and Department of Chemistry, Iowa State University, Ames, Iowa 50011. Received May 19, 1977

Abstract: The forward rate of the reaction $2\text{HCo}(\text{dmgH})_2\text{P}(n\text{-C}_4\text{H}_9)_3 = \text{H}_2 + 2\text{Co}(\text{dmgH})_2\text{P}(n\text{-C}_4\text{H}_9)_3$ has been determined in methanol-water solutions as a function of perchloric acid concentration, 0.003–0.10 M. The reaction proceeds by two parallel pathways, with respective first-order and second-order dependences upon the concentration of hydridocobaloxime. Once allowance is made for an H⁺-dependent equilibrium with $K_{\text{H}} = 1.3 \times 10^2 \text{ M}^{-1}$, which we interpret to be the protonation of oxime oxygens (a reaction known in related complexes), the first-order term proceeds at a rate directly proportional to [H⁺], and the second-order term is independent of [H⁺]. Deuterium labeling experiments were also carried out. The reaction appears to proceed by parallel heterolytic and homolytic cleavage of the hydrogen-cobalt bond.

Introduction

Hyrido complexes of cobalt(III) are conjugate acids of the corresponding cobalt(I) complexes. Thus Schrauzer and Holland¹ have isolated and characterized the hydride of bis-(dimethylglyoximate)cobalt (or cobaloxime). They find, that with an axial tri-*n*-butylphosphine base, the pK_a for transformation of H(Co)B to (Co)B⁻ is ~10.5 in 50% aqueous methanol (eq 1).



These two cobalt complexes are capable of independent existence and reactivity. For example, at pH ≥ 11 reaction with CH₂=CHX (X = CN, CO₂R, etc.; B = py) produces XCH₂CH₂Co(dmgH)₂B, whereas in neutral solution CH₃CH(X)Co(dmgH)₂B is formed.^{2,3} Similarly phenylacetylene reacts with DCo(dmgH)₂py to give stereospecific cis addition (eq 2), in contrast to the trans addition of the nucleophilic cobalt(I) anion.⁴

The deuterated complex, prepared from BD₄⁻ + ClCo^{III}(dmgH)₂py in MeOH, not MeOD, nevertheless transfers D to the organic substrate in reaction 2. This estab-