sequence, the energy for ionization of the iron ion in these complexes is dramatically lowered, thus rendering more accessible the iron(IV) oxidation state. The d-orbital energy levels must be directly related to the inductive effect of the axial σ-bonded group. This assumption is strengthened by the fact that half-wave potentials of +0.25 and +0.39 V are observed for $(OEP)Fe(n\text{-}C_4H_9)$ and $(C_{12}TPP)Fe(n\text{-}C_4H_9)$, respectively,[23] compared to potentials of +0.48 V for oxidation of $(OEP)Fe(C_6H_5)$ and +0.61 V for oxidation of $(TPP)Fe(C_6H_5)$.

The half-wave potential of the second oxidation appears to be insensitive to the nature of the axial ligand. This electron transfer takes place at E_{pa} = +1.43 V in CH_2Cl_2 or $E_{1/2}$ = +1.52 V in DME, 0.1 M TBA(PF_6), for $(TPP)Fe(C_6H_5)$ while the oxidation half-wave potential for (TPP)FeX occurs at $E_{1/2}$ = +1.40 V in CH_2Cl_2, 0.1 M TBA(ClO_4) (where X stands for an anionic halide or pseudohalide).[31] These observations suggest that the first oxidation of $(P)Fe(C_6H_5)$ effectively occurs at the metal center.

The electronic absorption spectra of the one-electron oxidized species obtained are in agreement with the above statement. For example, $[(OEP)Fe(C_6H_5)]^+$ does not exhibit any absorption band above 600 nm (see Table I and Figure 4a). In addition, the Soret band wavelength and molar extinction coefficients are very close to the corresponding values of the neutral complex, indicating that the removal of one electron from $(OEP)Fe(C_6H_5)$ does not affect the π system of the porphyrin. Furthermore, a sharp blue-shifted β band is observed in the spectrum. This absorbance is not found in any reported cation radical electronic absorption spectrum in the porphyrinic series. Consequently, one may describe these one-electron oxidized species as $[(P)Fe^{IV}(C_6H_5)]^+$.

Unusual Bond Lengths, Conformations, and Ligand Exchange Rates in B₁₂ Models with the Bis(salicylidene)-*o*-phenylenediamine Equatorial Ligand

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Abstract: Convenient synthetic procedures for B₁₂ models containing saloph (dianion of bis(salicylidene)-*o*-phenylenediamine) are reported. The crystal and molecular structure of two compounds containing pyridine (py) in one axial position are described. Compound I, $((py)Co^{III}(saloph)C_2H_5)\cdot H_2O$, $(C_{27}H_{24}CoN_3O_2\cdot H_2O)$, crystallizes in space group $P2_1/c$ with a = 12.140 (7) Å, b = 12.736 (8) Å, c = 15.822 (9) Å, β = 100.2 (1)°, V = 2407.7 Å³, D_{measd} = 1.37 (1) g cm⁻³, D_{calcd} = 1.38 g cm⁻³, and Z = 4. A total of 6319 reflections were measured. Compound II, $((py)Co^{III}(saloph)CH_2CN)\cdot H_2O$, $(C_{27}H_{21}CoN_4O_2\cdot H_2O)$, crystallizes in space group $P2_1/n$ with a = 13.964 (7) Å, b = 12.219 (7) Å, c = 14.903 (8) Å, β = 110.6 (1)°, V = 2380.3 Å³, D_{measd} = 1.42 (1) g cm⁻³, D_{calcd} = 1.43 g cm⁻³, and Z = 4. A total of 7532 reflections were measured. The structures were solved with conventional Patterson and Fourier methods. Block-diagonal least-squares refinement led to final R values of 0.035 and 0.049 for I and II, respectively. The most unusual structural feature in these compounds is the orientation of the py ligand of I in that it is positioned over the five-membered chelate ring made by the phenylenediamine moiety. This orientation has not been observed previously. The reason for this unusual orientation is discussed in terms of the very long Co–N(py) bond in I of 2.215 (4) Å, which is the longest bond found to date in any B₁₂ model. In II, this bond is shorter, 2.098 (4) Å, reflecting the weaker trans influence of CH_2CN compared to C_2H_5. The py lies over the six-membered chelate rings (the normal situation). The bond lengths and bond angles at the alkyl moiety are typical. However, the saloph moieties are distinctly nonplanar with the two salicylaldiminato units forming dihedral angles of −25.4 and 17.7° in I and II, respectively. Thus the distortions are in opposite directions. This difference can also be understood in terms of the Co–N bond lengths. These bond lengths are ∼0.1 Å longer than those found with comparable axial ligand sets in cobaloximes, where the equatorial ligand system comprises two dioximato ligands. Dynamic NMR methods allowed estimates of ligand exchange rates at 25 °C for compounds similar to II but with 3,5-lutidine (3,5-LUT). Two types of comparison were made. From reasonable estimates of exchange rates for the cobaloximes with the 3,5-LUT/CH₂CN ligand set, the reactivity of the saloph compound with these axial ligands is 10¹⁰ times as large. It is argued that this enormous cis influence is partly a ground-state effect and partly arises from the higher stability of saloph five-coordinate intermediates compared to cobaloxime five-coordinate intermediates. For example, the cobaloxime with the py/*i*-C₃H₇ axial ligand set has a Co–N bond length very similar to that of II. Yet the ligand exchange rate of the cobaloxime is estimated to be 10⁴ times less than that in II. The relevance of these findings to estimated Co–C bond dissociation energies (BDE) in models and to the Co–C bond homolysis reaction in B₁₂-dependent processes is discussed.

Introduction

Catalytic processes involving B₁₂-dependent enzymes are complex.[1] Proposed components of the mechanisms include formation of the holoenzyme–substrate complex (accompanied by confor-

mational changes in both the enzyme and B₁₂ coenzyme), homolytic cleavage of the Co–C bond, H atom abstraction from the substrate by the deoxyadenosyl radical formed by homolysis, substrate rearrangement to product (either via a radical pathway

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(1) "B₁₂"; Dolphin, D., Ed.; Wiley-Interscience: New York, 1982.

or possibly through a Co–C bonded intermediate), reformation of the deoxyadenosyl radical, and recycling of the process or termination by reformation of the uncleaved B$_{12}$ coenzyme. Many aspects of this general mechanism are unclear.[2] Approximately a dozen B$_{12}$ enzymes are known. These fall into several classes, often require other cofactors, and may utilize variations on this mechanism.[3] Two important unresolved issues are the following: In view of the relative inertness of the Co–C bond to thermolysis, why does the Co–C bond in the holoenzyme so readily cleave? How does the substrate rearrange and is a Co–C (substrate derivative) bond formed during this process?

Consideration of both of these important questions often involves the relationship between structure and Co–C bond energy.[2,4–7] *For the initial cleavage process*, the evidence that conformational changes occur on formation of the holoenzyme[8–10] has led to the consensus that structural distortions in the coenzyme induced by the interaction of the coenzyme (particularly its side chains) with the enzyme lead to cleavage.[11–13] The puckered corrin ring has some flexibility[14] and the most readily imagined Co–C bond weakening effect is a cis steric interaction between the corrin and the deoxyadenosine.[15] *For the rearrangement process*, arguments against reactive intermediates containing Co–C bonds have invoked steric hindrance. Alternatively, steric interaction between Co-bonded alkyl groups and the corrin could provide the driving force for rearrangement. Additionally, although success in finding biomimetic analogues of the B$_{12}$-catalyzed reaction has been limited, the few systems that have been found generally required Co.[16]

A clear need exists to gain a deeper understanding of the relationship between structure and Co–C bond stability and lability. No B$_{12}$ holoenzyme has been crystallized and structurally characterized. Also, the only reported alkylcobalamin structure is of coenzyme B$_{12}$ and work is now in progress to refine the structure of methylcobalamin (methyl B$_{12}$).[17]

Therefore, we have been following another approach, the structural elucidation of model compounds.[18–22] One class of models, namely, cobaloximes, which contain, in place of the corrin, the bis(dimethylglyoximato), or other bis(dioximato) moiety, has been extensively characterized.[18–20] The symmetry of these molecules permits the ready assessment of structural changes as the axial groups are systematically varied. For example, a

"butterfly" bending of the dioximes relative to each other can be characterized by the dioximato interplanar dihedral angle, α. Both the axial ligand and the lattice influence α, and such equatorial ligand conformational changes alter Co to axial ligating atom bond lengths and intraaxial ligand bond lengths and angles.

The Co–C bonds in cobaloximes are so stable that Co–C bond energies can be conveniently estimated in only selected cases.[2] Since a knowledge of the relationship between Co–C bond energies and structure is essential for a complete understanding of B$_{12}$-dependent processes, model systems containing more readily assessed Co–C bond energies are desirable candidates for study. Recently, Halpern and co-workers[2,5,6] reported that models containing the Schiff base ligand, saloph = dianion of bis(salicylidene)-*o*-phenylenediamine, had sufficiently weak Co–C bonds for reasonably convenient estimation of the bond dissociation energy. These complexes also appeared to be useful B$_{12}$ models in other ways. The neutral ligand trans to the alkyl is relatively labile, as found for cobalamins. Cobalamins have many properties intermediate between cobaloximes and Schiff base models,[2] and thus a deeper understanding of the latter, less frequently studied system appeared desirable.

Since no structural or ligand exchange rate data were available on Co^{III}(saloph) compounds, we initiated a program to prepare, structurally characterize, and study ligand exchange rates in some LCo(saloph)R complexes. Three-dimensional X-ray structures were determined for (py)Co(saloph)C$_2$H$_5$ (compound I) and (py)Co(saloph)CH$_2$CN (compound II), where py = pyridine. A remarkably long Co–N(py) bond was found for I, and the lability of the L ligand in compounds related to II is extraordinary. In addition, the plane of the pyridine ring in the ethyl derivative lies over the five-membered chelate ring, an orientation not previously observed for B$_{12}$ models. Convenient syntheses of LCo^{III}(saloph)R complexes are also described.

Experimental Section

Reagents. 1-Methylimidazole (Aldrich) was vacuum distilled (aspirator) and then recrystallized three times from the neat liquid at –60 °C. 3,5-Lutidine (Aldrich) was distilled under vacuum (aspirator). Chloroform-*d* (MSD Isotopes, 99.8 atom %d) was employed for ^{1}H NMR line shape studies. All other reagents were from Aldrich and were used without further purification.

Instrumentation. ^{1}H NMR lineshape measurements were made with an IBM WP-200SY NMR spectrometer operating at 200.13 MHz, equipped with a Bruker B-VT.1000 variable-temperature unit which maintained the sample within ±0.5°. ^{1}H NMR chemical shifts were determined with a Varian EM 390 (90 MHz) and referenced to Me$_4$Si.

^{1}H NMR Spectra. High quality ^{1}H NMR spectra were obtained from 0.05 M LCo(saloph)R solutions (CDCl$_3$, with an excess of L (0.017–0.042 M) for ^{1}H NMR exchange studies) subjected to 16 90° (3.7 μs) pulses with a relaxation delay of 8.0 s. Spectra were accumulated in the quadrature detection mode as 16K data points in the time domain which transformed to 8K data points in the frequency domain. Solvent deuterium was used for field frequency lock.
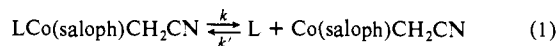
^{1}H NMR Line Shape Analysis. ^{1}H NMR line shapes were simulated by using a published program modified to be compatible with a UNIVAC UP-8180.[23]

Spectral observables used as parameters for line shape fitting (P_f and P_b, the relative populations of free and bound L (determined by integration of peak areas); T_{2f}' and T_{2b}', the spin–spin relaxation rate constants (related to the full peak width at half-height $w_{1/2} = 1/\pi T_2'$); and $\Delta\nu$, the chemical shift difference between the two sites (Hz)) were obtained from stopped-exchange, low-temperature spectra that contain well-resolved singlets for the methyl groups of free and coordinated L. The temperature range in which these parameters were determined was equal to or greater than the temperature range of the exchange measurements. P_f, P_b, T_{2f}', and T_{2b}' were independent of temperature in the stopped-exchange region.

For L = 3,5-lutidine $\Delta\nu$ was independent of temperature in the stopped-exchange region; however, $\Delta\nu$ varied linearly in this region for L = 1-methylimidazole and values for $\Delta\nu$ in the exchange region were determined by extrapolation.

The exchange constant τ ($\tau = P_f/k = P_b/k'$) (eq 1) was varied until the computer-simulated and experimental line shapes were visually identical.

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4480 *J. Am. Chem. Soc., Vol. 106, No. 16, 1984*

Summers et al.

$$LCo(saloph)CH_2CN \underset{k'}{\overset{k}{\rightleftharpoons}} L + Co(saloph)CH_2CN \qquad (1)$$

Preparations. Two general synthetic procedures were developed for LCo(saloph)R complexes. Method A was used when R contained an electron-withdrawing substituent. Otherwise, method B was used. All compounds with Co–C bonds were handled with minimal exposure to light to prevent photolytic cleavage of the Co–C bond.

Method A. LCo(saloph)CH₂CN (L = 1-methylimidazole, 3,5-lutidine). A magnetic stir bar and methanol (250 mL) were placed in a 500-mL Erlenmeyer flask and Co^{II}(saloph) (1.75 g, 4.7 mmol) added. Prepurified nitrogen was continuously bubbled through the stirred suspension. A NaBH₄ solution (0.8 g, 21 mmol) in 2 mL of H₂O) was slowly added. There was an immediate gas evolution and a color change from purple to green. ClCH₂CN (1.5 mL, 24 mmol) was added and the mixture stirred for 5 min. Acetone (50 mL) was then added, the N₂ purging was stopped, and the suspended solids were removed by suction filtration. The isolated solid was washed twice with acetone (10 mL) and discarded; the washings were added to the filtrate. Addition of L (50-fold molar excess) to the filtrate caused a color change from dark green to red. The volume was reduced to ~50 mL with a rotary evaporator. Crystallization of LCo(saloph)CH₂CN was induced by addition of water (~15 mL, or until the solution became turbid). Yields: 1.11 (48%) and 1.27 g (52%) for L = 1-CH₃IMID and 3,5-LUT, respectively. (1-CH₃IMID)Co(saloph)CH₂CN: ¹H NMR (CDCl₃, Me₄Si = 0.0 ppm) δ 8.26 (s, 2 H, N=CH), 7.90–6.36 (m, 15 H, saloph + IMID), 3.51 (s, 3 H, IMID-CH₃), 3.10 (s, 2 H, CoCH₂). Anal. Calcd for $C_{26}H_{22}N_5O_2Co$: C, 63.03; H, 4.48; N, 14.14. Found: C, 63.05; H, 4.53; N, 14.11. (3,5-LUT)Co(saloph)CH₂CN: ¹H NMR (CDCl₃) δ 8.30 (s, 2 H, N=CH), 8.00–6.42 (m, 15 H, saloph + 3,5-LUT), 3.16 (s, 2 H, CoCH₂), 2.08 (s, 6 H, 3,5-LUT-CH₃). Anal. Calcd for $C_{29}H_{25}N_4O_2Co$: C, 66.92; H, 4.84; N, 10.76. Found: C, 66.82; H, 4.88; N, 10.70.

This general procedure was used to prepare a variety of related compounds, including those containing L = 4-*tert*-butylpyridine, pyridine, and 4-(dimethylamino)pyridine and R = CH₂CF₃ and CH₂(C₆H₅). These were identified by NMR spectroscopy. Elemental analysis and ¹H NMR data are reported for (py)Co(saloph)CH₂CF₃. Anal. Calcd for $C_{27}H_{21}N_3O_2F_3Co$: C, 60.57; H, 3.95; N, 7.85. Found: C, 60.58; H, 3.99; N, 7.80. ¹H NMR (CDCl₃) δ 8.48 (d, 2 H, pyridine-Hα), 8.28 (s, 2 H, N=CH), 7.90–6.37 (m, 15 H, saloph + pyridine), 3.33 (q, ^3J(F–H) 15.8 Hz, 2 H, CoCH₂).

X-ray quality crystals of (py)Co(saloph)CH₂CN (prepared by using the above procedure) were obtained from acetone (0.3 g in 20 mL), followed by addition of water (~5 mL) and slow evaporation in the dark (2 days).

Method B. (py)Co(saloph)(neo-C₅H₁₁). Method A was followed except that C₅H₁₁I (1.5 mL) was employed, and L was not added to the filtrate. Instead, after the volume of the dark green solution was reduced to ~50 mL, water (~20 mL) was added to induce crystallization of the base-free (five-coordinate, solvato, or possibly dimeric) compound "Co(saloph)(neo-C₅H₁₁)". The purity was sufficient for further syntheses (yield 1.46 g). For analysis, large dark green crystals were obtained from an acetone–water mixture as described above.

Dissolution of the base-free compound in pyridine (0.5 g in 20 mL), filtration of the solution, and addition of water (~5 mL, or until the greenish black solution became turbid) gave a crystalline pyridine adduct in ~2 h (overall yield 1.47 g (~60%)).

Elemental analyses were obtained for the base-free compound (which crystallized with an equivalent of acetone) and the pyridine adduct. Co(saloph)(neo-C₅H₁₁)·(CH₃)₂CO: ¹H NMR (CDCl₃) δ 8.78 (s, 2 H, N=CH), 8.10–6.61 (m, 12 H, saloph), 2.87 (s, 2 H, CoCH₂), 2.12 (s, 6 H, acetone-CH₃), 0.64 (s, 9 H, neopentyl-CH₃). Anal. Calcd for $C_{28}H_{31}N_2O_3Co$: C, 66.92; H, 6.22; N, 5.57. Found: C, 66.69; H, 6.14; N, 5.50. (py)Co(saloph)CH₂C(CH₃)₃: ¹H NMR (CDCl₃) δ 8.79 (s, 2 H, N=CH), 8.64 (d, 2 H, py-Hα), 8.07–6.60 (m, 15 H, saloph + py), 2.90 (s, 2 H, CoCH₂), 0.63 (s, 9 H, neopentyl-CH₃). Anal. Calcd for $C_{30}H_{30}N_3O_2Co$: C, 68.83; H, 5.78; N, 8.03. Found: C, 68.84; H, 5.82; N, 8.02.
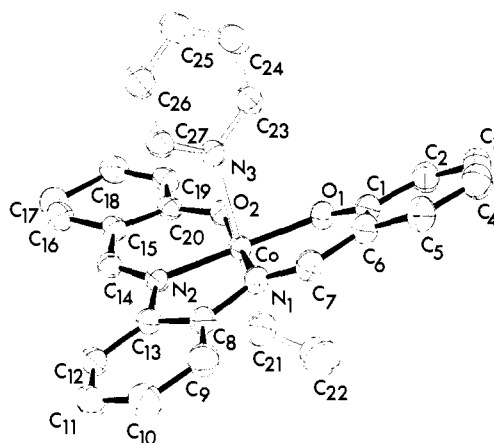
The compound (py)Co(saloph)C₂H₅ was prepared by using the above procedure except that C₂H₅I was employed. Method B was also used to prepare a variety of related compounds, including those containing the bases L = 4-*tert*-butylpyridine, 3,5-LUT, and 1-CH₃IMID and the alkyl groups R = CH₃, C₂H₅, *i*-C₃H₇, (only the base-free compound could be isolated), *i*-C₄H₉, *n*-C₃H₆CN, c-C₆H₁₁, CH₂C(CH₃)(COOC₂H₅)₂, and CH₂C(CH₃)(COOC₂H₅)(COSC₂H₅). These compounds were characterized by NMR spectroscopy.

X-ray quality crystals of (py)Co(saloph)C₂H₅ were obtained by dissolving the compound in py (0.3 g in 30 mL) and adding water (~5 mL, until the solution was slightly turbid) in the dark. Crystals were obtained in 1 day.

Crystal Data. Cell dimensions of crystals of I and II were determined

Table I. Crystallographic Data for Compounds I and II

	I	II
formula	$C_{27}H_{24}CoN_3O_2 \cdot H_2O$	$C_{27}H_{21}CoN_4O_2 \cdot H_2O$
mol wt	499.5	510.5
a, Å	12.140 (7)	13.964 (7)
b, Å	12.736 (8)	12.219 (7)
c, Å	15.822 (9)	14.903 (8)
β, deg	100.2 (1)	110.6 (1)
D_{measd}, g cm⁻³	1.37 (1)	1.42 (1)
D_{calcd}, g cm⁻³	1.38	1.43
Z	4	4
space group	$P2_1/c$	$P2_1/n$
μ, cm⁻¹	7.5	7.8
cryst dimens, cm³	0.07 × 0.05 × 0.01	0.08 × 0.06 × 0.10
no. of reflects measd	6319	7532
no. of independent reflects	2041	2859
max 2θ, deg (Mo Kα)	56	56
R	0.035	0.049

Figure 1. ORTEP drawing and numbering scheme for I.

from Weissenberg and precession photographs and refined on a single crystal diffractometer. Crystal data are given in Table I. One check reflection intensity was measured every 100 reflections during data collection. There was no systematic variation throughout the data acquisition. Cell dimensions and data collections for I and II were carried out on a SIEMENS AED and on a Philips PW 1100 diffractometer, respectively.

Solution and Refinement of Structures. The structures of both compounds were solved by conventional Patterson and Fourier methods and refined by the block-diagonal anisotropic least-squares methods to final R values of 0.035 for I and 0.049 for II. The contribution of hydrogen atoms was held constant (B = 5 Å²) in both structures. In the final refinement, the weighting scheme, $w = 1/(A + |F_o| + B|F_o|^2)$ where A = 14.7 (I) and 8.3 (II) and B = 0.01 for both I and II, was chosen so as to maintain $w(|F_o| - |F_c|)^2$ essentially constant over all ranges of F_o and $((\sin\theta)/\lambda)$ were given in ref 24. Atomic scattering factors utilized are given in ref 24. Final non-hydrogen positional parameters are collected in Table II. Hydrogen atom coordinates, anisotropic thermal parameters, and a list of final calculated and observed structure factors have been deposited. All calculations were done by using the computer programs from X-ray 70.[25]

Results

Preparation of Complexes. The preparation of LCo^{III}(saloph)R complexes has generally involved reduction of Co^{II}(saloph)[26] in anhydrous THF with sodium shot or amalgam, followed by addition of alkyl halide at -78 °C.[27-30] Unless care is exercised,

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Table II. Atomic Coordinates ($\times 10^4$) of Non-Hydrogen Atoms of Compounds I and II

|	I				II		
	x	*y*	*z*		*x*	*y*	*z*
Co	3029 (1)	1469 (0)	2000 (0)	Co	5921 (0)	4272 (1)	2629 (0)
O(1)	2460 (2)	2325 (2)	1040 (2)	O(1)	4930 (2)	5073 (3)	1645 (2)
O(2)	4444 (3)	2065 (2)	1912 (2)	O(2)	6767 (3)	4493 (3)	1886 (2)
N(1)	1654 (3)	808 (3)	2056 (2)	N(1)	5091 (3)	4109 (3)	3384 (3)
N(2)	3604 (3)	602 (3)	2952 (2)	N(2)	6874 (3)	3380 (3)	3559 (2)
N(3)	3365 (3)	234 (3)	1094 (2)	N(3)	5347 (3)	2832 (3)	1862 (3)
C(1)	1482 (4)	2229 (4)	562 (3)	C(1)	4090 (4)	5492 (4)	1690 (3)
C(2)	1204 (4)	2885 (4)	−186 (3)	C(2)	3482 (5)	6155 (5)	919 (4)
C(3)	212 (4)	2774 (5)	−741 (4)	C(3)	2565 (5)	6595 (6)	908 (5)
C(4)	−585 (5)	2043 (5)	−599 (4)	C(4)	2207 (6)	6387 (7)	1663 (5)
C(5)	−380 (4)	1431 (5)	119 (3)	C(5)	2771 (5)	5750 (7)	2411 (5)
C(6)	639 (4)	1495 (4)	719 (3)	C(6)	3721 (4)	5306 (5)	2452 (4)
C(7)	765 (4)	843 (4)	1464 (3)	C(7)	4228 (4)	4601 (5)	3250 (4)
C(8)	1690 (4)	175 (4)	2809 (3)	C(8)	5513 (4)	3361 (4)	4161 (3)
C(9)	774 (4)	−316 (4)	3063 (3)	C(9)	5051 (4)	3063 (5)	4822 (4)
C(10)	941 (5)	−885 (5)	3826 (4)	C(10)	5547 (5)	2284 (6)	5515 (4)
C(11)	1994 (5)	−954 (4)	4336 (3)	C(11)	6472 (5)	1827 (5)	5565 (4)
C(12)	2896 (4)	−469 (4)	4083 (3)	C(12)	6939 (4)	2146 (4)	4924 (3)
C(13)	2751 (4)	89 (3)	3309 (3)	C(13)	6461 (3)	2937 (4)	4233 (3)
C(14)	4659 (4)	415 (3)	3245 (3)	C(14)	7808 (3)	3154 (4)	3601 (3)
C(15)	5560 (4)	901 (4)	2932 (3)	C(15)	8271 (3)	3584 (4)	2966 (3)
C(16)	6670 (4)	562 (4)	3288 (3)	C(16)	9315 (4)	3320 (5)	3161 (4)
C(17)	7589 (4)	1015 (5)	3066 (4)	C(17)	9847 (4)	3745 (5)	2621 (4)
C(18)	7448 (4)	1845 (5)	2486 (3)	C(18)	9348 (4)	4458 (5)	1860 (4)
C(19)	6400 (4)	2204 (4)	2116 (3)	C(19)	8319 (4)	4694 (5)	1628 (4)
C(20)	5416 (4)	1731 (5)	2309 (3)	C(20)	7751 (4)	4268 (4)	2166 (3)
C(21)	2820 (6)	2633 (5)	2845 (4)	C(21)	6454 (4)	5680 (4)	3304 (4)
C(22)	1849 (7)	3233 (7)	2659 (5)	C(22)	6904 (4)	5583 (4)	4336 (4)
C(23)	3528 (5)	−778 (4)	1323 (3)	C(23)	4411 (4)	2457 (4)	1723 (3)
C(24)	3743 (6)	−1563 (4)	774 (3)	C(24)	4027 (4)	1496 (5)	1234 (4)
C(25)	3799 (6)	−1325 (5)	−51 (3)	C(25)	4641 (5)	905 (4)	869 (4)
C(26)	3604 (6)	−292 (5)	−317 (3)	C(26)	5604 (5)	1287 (6)	997 (5)
C(27)	3405 (4)	461 (4)	263 (3)	C(27)	5926 (4)	2249 (5)	1499 (4)
O(3)	4373 (3)	3414 (3)	400 (2)	O(3)	4148 (3)	3902 (3)	−233 (3)
				N(4)	7239 (4)	5479 (4)	5152 (3)
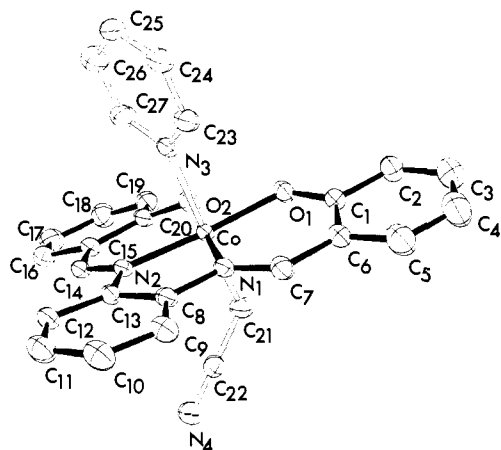
Figure 2. ORTEP drawing and numbering scheme for II.

the product is often contaminated with Co¹¹(saloph). A different procedure involving PdCl₂-catalyzed NaBH₄ reduction was effective for primary alkyls only.[26] In general, base-free species are isolated since the six-coordinate complexes lose pyridine slowly. The convenient procedures described in the Experimental Section allowed us to isolate a large series of compounds. Although crystals of many of these could be grown, the compounds lose pyridine readily.

Structure. ORTEP drawings of I and II with the atom numbering scheme are depicted in Figures 1 and 2, respetively. Bond lengths are listed in Table III.

The cobalt atom in both I and II exhibits distorted octahedral stereochemistry. The saloph ligand occupies the four equatorial positions. Respective bond lengths in the Co(saloph) units of both compounds are equal within experimental error. The cobalt atom is nearly in the plane of the four N donors, which are coplanar within ±0.02 (I) and ±0.05 Å (II), and is displaced by 0.03 (I)

and 0.05 Å (II) from the plane toward the axial carbon atom. The CH₃CH₂–Co–N(py) fragment in I is characterized by Co–C and Co–N bond lengths of 2.042 (6) and 2.215 (4) Å and by C–Co–N and Co–C–C angles of 176.5 (2) and 117.3 (5)°, respectively. The corresponding values for II are 1.995 (5) and 2.098 (4) Å, and 177.4 (3) and 114.2 (4)°, respectively. The C–C bond length of 1.39 (1) Å of the axial ethyl group in I is particularly short, even allowing for its large esd (see below). The CH₂–CN and CH₂C–N bond lengths of 1.447 (7) and 1.146 (7) Å as well as the CH₂–C–N angle of 177.8 (6)° are in the range observed for cyanomethylcobaloximes PR₃Co(DH)₂CH₂N (where DH = monoanion of dimethylglyoxime).[31,32] The overall geometry of the Co(saloph) unit is significantly distorted from planarity in both I and II but the nature of the distortion differs. In I the two salicylaldiminato residues are bent toward pyridine and assume a symmetric umbrella-shape conformation (the interplanar dihedral angle α is −25.4°) with a slight tilt of the planes of the aromatic rings. Consequently the bridging phenylene ring bends away from the pyridine to preserve the approximately trigonal geometry around N(1) and N(2). The side view of the molecule depicted in Figure 3a clearly shows the above deformations.

The orientation of the axial ligands with respect to the Schiff base is shown in Figure 4a. The pyridine plane is only slightly rotated with respect to the N(2)···O(1) direction, whereas the CH₂–CH₃ bond lies between the O(1) and N(1) atoms. Some interplanar angles are reported in Table IV.

In II the salicylaldiminato residues are analogously bent to a symmetric umbrella ($\alpha = +17.7°$), but away from pyridine, with a slight twist between the planes of the aromatic rings. Thus the whole equatorial ligand assumes a flat helical conformation as shown in Figure 3b. On the other hand, the bridging phenylene ring bends toward the pyridine. The interplanar angles (Table

(31) Bresciani-Pahor, N.; Randaccio, L.; Summers, M.; Toscano, P. J. *Inorg. Chim. Acta* **1983**, *68*, 69.

(32) Bresciani-Pahor, N.; Randaccio, L., unpublished results.

Table III. Bond Lengths (Å) and Angles (deg) for Compounds I and II

	I	II
Co–N(3)	2.215 (4)	2.098 (4)
Co–C(21)	2.042 (6)	1.999 (5)
Co–O(1)	1.898 (3)	1.896 (3)
Co–O(2)	1.905 (3)	1.902 (4)
Co–N(1)	1.885 (4)	1.888 (5)
Co–N(2)	1.898 (3)	1.892 (3)
O(1)–C(1)	1.296 (5)	1.303 (6)
C(6)–C(7)	1.429 (7)	1.437 (7)
C(7)–N(1)	1.298 (5)	1.298 (7)
N(1)–C(8)	1.433 (6)	1.429 (6)
C(13)–N(2)	1.423 (6)	1.430 (7)
N(2)–C(14)	1.305 (6)	1.313 (6)
C(20)–O(2)	1.305 (5)	1.316 (6)
C(21)–C(22)	1.392 (11)	1.447 (7)
C(22)–N(4)		1.146 (7)
N(3)–C(23)	1.344 (6)	1.330 (7)
N(3)–C(27)	1.355 (6)	1.328 (8)
N(3)–Co–C(21)	176.5 (2)	177.4 (2)
O(1)–Co–O(2)	85.3 (1)	84.9 (2)
O(1)–Co–N(1)	95.4 (1)	94.7 (2)
O(1)–Co–N(2)	179.4 (2)	175.9 (2)
O(1)–Co–N(3)	88.4 (1)	88.7 (1)
O(1)–Co–C(21)	92.1 (2)	89.2 (2)
O(2)–Co–N(1)	176.7 (2)	177.8 (2)
O(2)–Co–N(2)	94.6 (1)	95.0 (2)
O(2)–Co–N(3)	87.9 (1)	89.9 (2)
O(2)–Co–C(21)	88.7 (2)	88.5 (2)
N(1)–Co–N(2)	84.7 (2)	85.6 (2)
N(1)–Co–N(3)	88.9 (2)	92.2 (2)
N(1)–Co–C(21)	94.6 (2)	89.4 (2)
N(2)–Co–N(3)	91.0 (1)	87.2 (1)
((2)–Co–C(21)	88.5 (2)	95.0 (2)
Co–C(21)–C(22)	117.3 (5)	114.2 (4)
C(21)–C(22)–N(4)		177.8 (6)
Co–N(3)–C(23)	122.8 (3)	122.7 (4)
Co–N(3)–C(27)	121.2 (3)	120.1 (3)
C(23)–N(3)–C(27)	116.0 (4)	117.2 (4)

**Table IV.** Interplanar Angles of Interest in I, II, and Co^{II}(saloph)

planes[a]	interplanar angle, deg			
	I[b]	II[b]	Co(II) (saloph)[c]	
1–3	−12.1	+8.8	4.4	3.0
1–5	−12.1	+7.6	6.0	1.1
305	−24.2	+16.2	10.0	4.2
1–4	+9.5	−9.5	3.4	1.3
1–7	−12.8	+7.6	4.4	3.4
1–8	−12.9	+9.8	6.1	0.8
7–8	−25.4	+17.7	10.4	2.8

[a] Planes are defined as follows: 1, O(1), O(2), N(1), N(2); 2, C-(1)–C(6); 3, O(1), N(1), C(1), C(6), C(7); 4, C(8)–C(13); 5, O(2), N(2), C(14), C(15), C(20); 6, C(15)–C(20); 7, 3(1), N(1), C(1)–C(7); 8, O(2), N(2), C(14)–C(20). [b] In the case of I and II, the sign − refers to bending toward the axial pyridine group and the sign + toward the alkyl group. [c] The two values reported refer to two different crystalline forms, the first being orthorhombic, the other monoclinic.[33]

IV) are smaller than those reported for I, but of opposite sign when referenced with respect to the axial ligands. The orientation of the axial ligands with respect to the Co(saloph) unit is shown in Figure 4b. These orientations are nearly interchanged with those of the axial ligands in I. In fact, the pyridine plane is nearly parallel to the N(1)···N(2) direction, whereas the cyanomethyl group lies between the N(1) and N(2) atoms.

Bond lengths and angles of the Co(saloph) unit in I and II are very similar to those reported[33] for Co^{II}(saloph), with the exception of the coordination distances. The Co(III)–N and Co(III)–O distances (mean values in I and II of 1.891 (4) and 1.901 (3) Å, respectively) are longer than the respective values (1.873 (5) and 1.843 (4) Å) of the four-coordinate Co(II) complex. A similar

(33) Bresciani-Pahor, N.; Calligaris, M.; Delise, P.; Dodic, G.; Nardin, G.; Randaccio, L. *J. Chem. Soc., Dalton Trans.* **1976**, 2478.
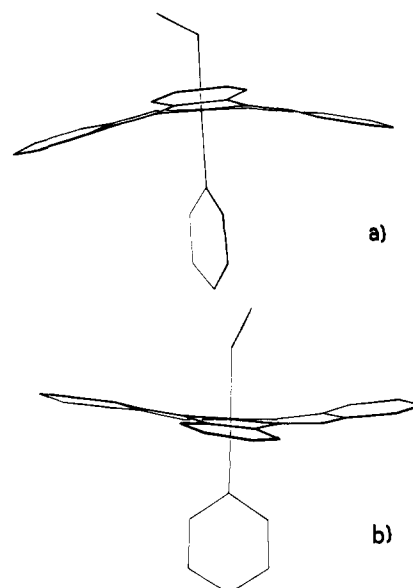
Figure 3. A side view of the molecules of I (a) and of II (b).
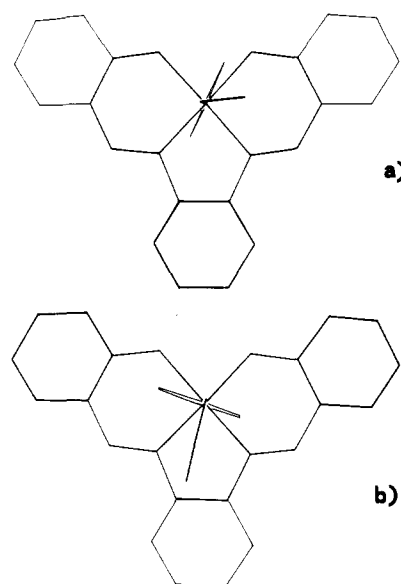
Figure 4. Projection on the coordination plane of the molecules of I (a) and II (b).

shortening is observed in other cobalt complexes having salen-type tetradentate equatorial ligands (salen = dianion of bis(salicylidene)ethylenediamine). The mean Co(II)–N and Co(II)–O bond lengths in four-coordinate complexes are 1.865 and 1.865 Å, whereas the Co(III)–N and Co(III)–O are 1.883 and 1.897 Å, respectively, in the octahedral complexes.[34–36] Furthermore, the distortions of the Co(saloph) unit in I and II are significantly larger than those reported for Co^{II}(saloph). Comparison of the most relevant interplanar angles (Table IV) shows that the presence of axial ligands provokes large distortions in the equatorial Schiff base.

Crystal Packing. The crystals of I consist of discrete molecules which bind a water molecule at O(3), through two hydrogen bonds involving O(1) and O(2) with distances at 3.029 (5) and 2.935 (5) Å, respectively. No other hydrogen bonds have been detected. For II, two (py)Co(saloph)CH$_2$CN and two water molecules are arranged around the $^1/_2$, $^1/_2$, O symmetry center to form a dimeric unit held by hydrogen bonds between water molecules and the

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(35) Schaefer, W. P.; Marsh, R. E. *Acta Crystallogr., Sect. B* **1969**, *B25*, 1675.

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Ligand Exchange Rates in B₁₂ Models

J. Am. Chem. Soc., Vol. 106, No. 16, 1984 4483

Table V. Ligand Exchange Rate Data from Dynamic NMR

P_f	P_b	E_a, kcal/mol	ln A	k_{298}, s⁻¹
		(1-CH₃IMID)Co(saloph)CH₂CN		
0.650	0.350	19.4'	40.2	1.52×10^3
0.390	0.610	18.0	37.5	1.22×10^3
0.827	0.173	16.7	35.5	1.33×10^3
averages		18.0 ± 1.3	37.7 ± 2.4	$(1.36 \pm 0.15) \times 10^3$
		(3,5-LUT)Co(saloph)CH₂CN		
0.660	0.340	18.6	41.5	2.44×10^4
0.642	0.358	17.7	39.8	2.06×10^4
averages		18.2 ± 0.6	40.7 ± 1.2	$(2.25 \pm 0.27) \times 10^4$

Table VI. Comparison of Structural Parameters of Some (py)Co(Schiff base)R and (py)Co(DH)₂R Compounds

	Co-N, Å	Co-C, Å	NCoC, deg	α,[a] deg
(py)Co(saloph)-CH₂CH₃[b]	2.215 (4)	2.042 (6)	176.5 (2)	−25.4
(py)Co(saloph)-CH₂CN[b]	2.098 (4)	1.999 (5)	177.4 (2)	+17.7
(py)Co(DH)₂-CH₂CH₃[c]	2.084 (7)	2.060 (10)		~0
(py)Co(DH)₂-CH₂NO₂[d]	2.028 (3)	2.002 (3)	176.0 (1)	~0
(py)Co(salen)-CH=CH₂[e]	2.119 (10)	1.93 (2)		+16.8
(py)Co(salpn)-CH(CN)₂[f]	2.060 (9)	2.02 (1)	174.9 (4)	+23.8

[a] α is the interplanar angle between planes 7 and 8 as described in Table IV except for the last entry, where it is the interplanar angle between the two terminal aromatic rings. [b] Present work. [c] Ref. 39. [d] Ref. 40. [e] Ref. 43. [f] Ref. 42.

Figure 5. Calculated and observed ¹H NMR spectra of the methyl resonance for free (downfield) and bound 1-CH₃IMID as a function of temperature ([(1-CH₃IMID)Co(saloph)CH₂CN] ≈ 0.05 M; [1-CH₃IMID] ≈ 0.03 M; CDCl₃).

oxygen atoms of the saloph ligand. Specifically, the water molecule, at O(3), forms a hydrogen bond to O(1), (2.987 (5) Å and two additional bonds to the O(1)' and O(2)' atoms of the saloph unit related by the symmetry center. The latter distances are 3.092 (6) and 3.055 (5) Å, respectively.

Dynamic NMR Data. Results of ligand exchange studies for the complexes LCo(DH)₂CH₂CN, L = 1-CH₃IMID and 3,5-LUT, are summarized in Table V, see also Figure 5. For both complexes, k (eq 1) was independent of P_f and P_b (Table V), suggesting that ligand exchange in CDCl₃ proceeds via an S_N1 LIM mechanism, as found for related cobaloxime complexes.[32,33] Thus $k = k_1$, where k_1 is the first-order ligand dissociation rate constant (see eq 2–4, Discussion).

Activation parameters in Table V and the room-temperature dissociation rate constant were determined by linear least-squares analysis of the ln k_1 vs. $1/T$ data (see figure, supplementary material).

Discussion

Structural Comparison. Three noteworthy features of the (py)Co^{III}(saloph)C₂H₅ structure are (a) the Co-N(py) bond length, which is the longest found to date in a B₁₂ model compound, (b) the orientation of the pyridine above the five-membered chelate ring, and (c) the large distortion of the saloph ligand away from the ethyl group. All three structural features are interrelated and can be explained with the following new hypothesis: The bulkier of the two axial ligands will be over a six-membered chelate ring as shown in Figure 4.

First consider the bulk of the ethyl group. Although the bending in II is toward the cyanomethyl group, the Co-C bond length of 1.999 (5) Å is slightly but significantly shorter than that of 2.042 (6) Å in I and the Co-CH₂-R angle of 114.2 (4)° in II is smaller than that of 117.3 (5)° in I.

The geometry of the Co-CH₂-R fragment in I and II is very close to that of similar derivatives of cobaloximes, namely, (py)Co(DH)₂C₂H₅[39] and (py)Co(DH)₂CH₂NO₂[40] where the corresponding figures are 2.060 (10) Å and 122.4 (8)° and 2.002 (6) Å and 113.7 (2)°, respectively. A shorter Co-C distance of 1.990 (7) Å but a similar Co-CH₂-CH₃ angle of 119.5 (7)° has been reported for the dimer [Co(salen)C₂H₅]₂.[41] The CH₂-CH₃ bond length of 1.471 (9) Å in the latter compound is consistent with an increase of s character in the CH₂ orbital involved in the C-C bond, since the Co-CH₂-CH₃ angle is larger than tetrahedral. A similar shortening of the CH₂-CH₃ distance is found for I. However, the low value of 1.39 (1) Å must arise partly from the thermal motion of the C(21) and C(22) atoms. Thus, there is nothing unusual about the ethyl group in I.

Likewise, the bond lengths and bond angles within the pyridine ligand are normal. However, the combined cis and trans influences in I increase the Co-N bond length to the point that the *effective* bulk of the py is decreased to the point that it is less bulky than the ethyl group. If one accepts the above hypothesis, then the ethyl group in I prefers to lie over a six-membered chelate ring of saloph (Figure 4a). Steric interaction in this orientation induces bending of the salicylaldiminato residues toward pyridine. As a consequence, the phenylene bridge bends toward the ethyl group and the pyridine adopts the observed orientation. In II, the pyridine is the bulkier axial ligand (the normal situation). Its preferred orientation is over the saloph six-membered chelate rings. Consequently, the direction of saloph bending in II is opposite to that in I (Figure 4b).

Known Co-N(py) bond lengths, in octahedral cobalt(III) Schiff base complexes related to I and II, range from 2.060 (9) Å in (py)Co(salpn)CH(CN)₂[42] (salpn = dianion of bis(salicylilidene)-1,2-propanediamine) to 2.119 (10) Å in (py)Co(salen)-CH=CH₂.[43] Furthermore, the two halves of the equatorial ligand bend away from the pyridine, making interplanar angles of about 20°. An even longer Co-N bond of 2.16 (1) Å has been reported

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(43) Calligaris, M.; Nardin, G.; Randaccio, L. *J. Chem. Soc. A* **1972**, 1433.

for (py)Co(acacen)CH$_3$[44] (acacen = dianion of bis(acetyl-acetone)ethylenediimine). The two halves of the equatorial ligand have an interplanar angle of 6°. A shorter Co–N(py) bond of 2.031 (9) Å is found in (py)Co(salen)OCH$_3$.[45]
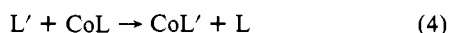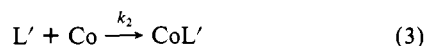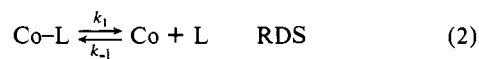
Finally, values of the Co–N(py) distances in the range 2.028 (3)–2.099 (2) Å have been reported for (py)Co(DH)$_2$R.[18,40] In none of these complexes does the pyridine lie over a five-membered ring of the equatorial ligand, as in I.

We believe this unusual py orientation exists because of the large cis influence of the saloph ligand. Pertinent results are summarized in Table VI for related systems. It is clear from this table that the Co–N bonds are much larger in Schiff base complexes compared to cobaloximes but that the Co–C bond lengths are relatively unaffected. This trend, based on fewer examples, has been noted previously.[46]

This cis influence is consistent with the observation that five-coordinate Co(Schiff base)R complexes are readily isolated[27] in comparison to cobaloximes, for which no well-documented five-coordinate species appears stable. (The structure of the five-coordinate species Co(acacen)CH$_3$ has been reported.[48]) An additional factor in the stability of five-coordinate Schiff base B$_{12}$ model complexes could be the flexibility of the equatorial ligand system that permits shorter and presumably more stable Co–C bonds. The energy required for an analogous distortion in cobaloximes may be too large to permit ready isolation of five-coordinate species. Several discussions of possible factors influencing the stability of five-coordinate organocobalt complexes have appeared.[41,48,49] An important consequence of the stability of such five-coordinate Schiff base complexes is the increased lability toward neutral axial ligand exchange (as described below).

Finally, the Co–N(5,6-dimethylbenzimidazole) bond length in coenzyme B$_{12}$ (deoxyadenosylcobalamin) is 2.24 Å.[14] This is the longest bond of this type reported to date. The cobalamin structure is complex, and a simple parameter such as α is not available to summarize distortions succinctly. However, the benzimidazole and deoxyadenosyl ligands lie over six-membered chelate rings. Although this orientation is in keeping with arguments made above, it cannot be attributed only to steric interaction with the corrin ring since both the attachment of the benzimidazole to the corrin via a complex bridge and the amide side chains on the corrin may dictate the orientation of the 5,6-dimethylbenzimidazole. The long bond, however, is probably largely a consequence of normal cis and trans influences since a much shorter bond is observed in vitamin B$_{12}$ (cyanocobalamin) where the bridge and side chains are also present.

The Co–N Axial Bond Lability. Cobaloxime ligand exchange rates can be studied by using classical methods, and, in noncoordinating solvents, eq 2–4 for an S$_N$1 LIM mechanism account

$$\text{Co–L} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{Co} + \text{L} \qquad \text{RDS} \qquad (2)$$

$$\text{L}' + \text{Co} \overset{k_2}{\longrightarrow} \text{CoL}' \qquad (3)$$

$$\text{L}' + \text{CoL} \rightarrow \text{CoL}' + \text{L} \qquad (4)$$

for the results for a variety of leaving, entering, and alkyl ligands.[36,37] The putative five-coordinate intermediate is nonselective (i.e., competition ratios $k_{-1}/k_2 \approx 1$ for nonbulky and non-hydrogen-bonding[15] L and L') and therefore very reactive. The value for k_1 reflects the length of the Co–N bond for a series of (py)-Co(DH)$_2$R complexes.[50]

The dynamic NMR studies described here are also consistent with a dissociative process for LCo(saloph)R complexes in noncoordinating solvents. Competition ratios cannot be determined by the NMR method, and we cannot assess the reactivity of the five-coordinate intermediate. However, we believe it must be more stable than the analogous Co(DH)$_2$R intermediate, since formation constants for LCo(saloph)R are less than for LCo(CH)$_2$R. Indeed, as we will now argue, the difference in reactivity between the two model systems is too large to be solely a ground-state effect.

For (py)Co(DH)$_2$(i-C$_3$H$_7$), k_1 is ~3 s^{-1} (25 °C)[50] and Co–N-(py) is 2.099 Å.[18] For (3,5-LUT)Co(saloph)CH$_2$CN, k_1 is ~2 × 10^4 s^{-1} (extrapolated to 25 °C) and Co–N is 2.098 Å in the py analogue. Thus, although the bond lengths are nearly the same, the saloph system is ~10^4 times more reactive. Our studies on the dependence of R of LCo(DH)$_2$R ligand exchange rates indicate that complexes with bulky R groups, such as i-C$_3$H$_7$, are ~10 times more reactive than expected on the basis of studies with less bulky R groups. Therefore, the 10^4 ratio must be considered to be a conservative estimate. We can also estimate that k_1 for (3,5-LUT)Co(DH)$_2$CH$_2$CN is ~5 × 10^{-6} s^{-1}.[15] This value compares to ~2 × 10^4 s^{-1} for (3,5-LUT)Co(saloph)CH$_2$CN. *The cis effect of saloph is then about 10^{10}!* Perhaps 10^5 of this factor is a ground-state effect due to the long C–N bond and 10^5 is due to the stability of five-coordinate Co(saloph)R.

Very little systematic data exist for further rate comparisons. Dynamic NMR studies by Brown and co-workers[38] indicate that the Co(acacen) system is very reactive, followed by Co–corrin systems, followed by cobaloximes. A close comparison of rates is hampered by the use of widely different temperature ranges.

In *preliminary* studies, we have attempted to make a more specific comparison of cobalamin systems. Stopped-flow studies of the rate of dissociation of 5,6-dimethylbenzimidazole in cyanomethylcobalamin (induced by N(3) protonation)[51] give a rate constant of ~10^2 s^{-1} at 0 °C. The extrapolated value for (3,5-LUT)Co(saloph)CH$_2$CN is ~10^3 s^{-1} at this temperature. The 3,5-LUT is probably a poorer leaving ligand than 5,6-dimethylbenzimidazole. Nevertheless, by the criterion of ligand dissociation rates, the Co(saloph) system is a much better cobalamin model than the cobaloximes, which are about 10^7 less reactive than comparable cobalamines.[52]

Co–C Bond Lability. Halpern has examined the influence of trans ligands on Co–C BDE estimated by a kinetic method[2,5,6] and found that weaker trans donor ligands lead to weaker Co–C bonds. This weakening can involve no steric changes such as in the substitution of electron-withdrawing groups at the 4-position of pyridine or steric changes such as the introduction of substituents at the 2-position of pyridine. In Halpern's studies, weaker bonds are found for cobaloximes with 2-substituted pyridines and for (py)Co(saloph)R complexes. We have shown that rather than distorting the equatorial ligand system, 2-substituted pyridine cobaloximes have very long Co–N(pyridine) bonds.[15] We demonstrate here that (py)Co(saloph)R complexes also have very long bonds, almost as long as in coenzyme B$_{12}$ itself.

The conformational change of the coenzyme in the holoenzyme could possibly invole a lengthening of the Co–N(benzimidazole) bond, a suggestion we have made previously.[15] Such a change decreases the overlap of the N-donor orbital with the Co orbitals of appropriate symmetry. As demonstrated in Halpern's studies, this decreased electron donation by the axial N donor will facilitate Co–C bond cleavage.

The most widely held view of the enzyme conformational change is that a corrin ring distortion would enhance steric repulsion between the deoxyadenosyl and the corrin ring, directly weakening

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(51) The measurement of Co–N(benzimidazole) dissociation under acid conditions is complex. See for example: Reenstra, W. W.; Jencks, W. P. *J. Am. Chem. Soc.* **1979**, *101*, 5780. Brown, K. L.; Awtrey, A. W.; Chock, P. B.; Rhee, S. G.; In "Vitamin B$_{12}$"; Zagalak, W. F., Ed.; Walter de Gruyter & Co.: New York, 1979.

(52) It is of some interest that this same factor of 10^7 is found for NCS substitution comparing cobaloximes (Hague, D. N.; Halpern, J. *Inorg. Chem.* **1967**, *6*, 2059) to cobalamins (Randall, W. C.; Alberty, R. A. *Biochemistry* **1966**, *5*, 3189. Randall, W. C.; Alberty, R. A. *Ibid.* **1967**, *6*, 1520). We thank a reviewer for pointing out this similarity.

Ligand Exchange Rates in B_{12} Models

J. Am. Chem. Soc., Vol. 106, No. 16, 1984 4485

the Co–C bond. However, alternatively or additionally, such a corrin ring conformational change could lead to an increased Co–N(benzimidazole) bond length that in turn would facilitate Co–C bond homolysis.

Although Co–C bond lability is a function of the equatorial ligand system, we have found no evidence that Co–C bond lengths are a function of the equatorial ligand. This may be because the primary determinant of Co–C bond lengths may be steric interactions of the alkyl with the equatorial ligating atoms all of which are similar in size (N, O).[53] Thus, if the alkyl ligand is of low bulk, such as CH_3 or C_2H_5, either a change in the equatorial ligand or in the trans ligand has little influence on Co–C bond length.

Estimates of Co–C bond energies for a series of (py)Co(saloph)R compounds reveal that these bond energies decrease as R group bulk increases.[5] The instability of compounds with R groups larger than C_2H_5 has thus far prevented our obtaining suitable crystals. However, the similarity of relevant geometric parameters at the ligating C for a variety of equatorial ligand system leads us to predict with confidence that Co–C bond lengths will increase in LCo(saloph)R complexes as the bulk of R increases.

Summary

We have shown that there is a distinct parallel between weak Co–C bonds, as estimated by others,[2,5,6] and long trans Co–N bonds. The Co–N lability in Co(saloph) compounds that cannot be explained solely on the grounds of the long Co–N bonds probably reflects the stability of the five-coordinated intermediate. Consideration of the length of the Co–N axial bond length and preliminary ligand exchange rates of cobalamins suggest that Co(saloph) compounds are much better models than cobaloximes. Finke[54-56] has argued that a hybrid Schiff base/dioxime model,

often referred to as the Costa model,[57] may better reflect the properties of cobalamins. In any case, a complete understanding of the factors that influence the properties of such complex molecules as cobalamins requires a detailed study of a broad range of model compounds. In this regard, more estimates of Co–C BDE's would be welcome. Finally, this work clearly establishes that the *cis influence* is a function of the *trans influence*. When X is a weak trans labilizer such as OCH_3, the bond trans to X is of comparable length in a variety of systems. When X is a strong trans labilizer such as C_2H_5, then the increased cis influence of ligand such as saloph is most readily apparent. To our knowledge, this relationship of the cis influence to the trans influence in organocobalt compounds has not been previously recognized.

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