

Rare Examples of Structurally Characterized Five-Coordinate Organocobalt Complexes. Novel Dynamic NMR Evidence for Synergistic Enhancement of Cis and Trans Effects in B₁₂ Models

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Abstract: A major factor influencing Co-C bond stability both in B₁₂ compounds and organocobalt B₁₂ models appears to be the coordination number. Five-coordinate complexes are unusually stable to Co-C bond thermolysis, but structurally characterized examples of five-coordinate organocobalt complexes are rare. None are known for cases where R is a bulky group, such as *i*-C₃H₇. We report two definitive examples of five-coordinate complexes of the type Co(saloph)R, where saloph = dianion of disalicylidene-*o*-phenylenediamine. The structure of one species (R = *i*-C₃H₇) permits the first assessment of the effects of R bulk on the structure and also provides insight into the structural basis for the thermal stability of the species of reduced coordination number. We have also characterized the third example of a six-coordinate organocobalt saloph compound. Specifically, the crystal and molecular structures of Co(saloph)-*i*-C₃H₇·1.5H₂O (I), Co(saloph)CH₃·0.5H₂O (II), and pyCo(saloph)CH₂CF₃ (py = pyridine) (III) are described. Compounds I and III are pentacoordinate and hexacoordinate, respectively, while crystals of II are comprised of both pentacoordinate and dimeric molecules. Crystallographic details follow. I: C₂₃H₂₁CoN₂O₂·1.5H₂O, space group *Pbcn*, *a* = 26.075 (6) Å, *b* = 9.617 (3) Å, *c* = 16.109 (3) Å, *D*_{calcd} = 1.46 g cm⁻³, *Z* = 8, *R* = 0.057 for 5437 measured reflections. II: C₂₁H₁₇CoN₂O₂·0.5H₂O, space group *P1̄*, *a* = 12.100 (8) Å, *b* = 20.392 (9) Å, *c* = 11.606 (8) Å, *α* = 53.3 (1)°, *β* = 127.6 (1)°, *γ* = 121.7 (1)°, *D*_{calcd} = 1.50 g cm⁻³, *Z* = 4, *R* = 0.041 for 7360 measured reflections. III: C₂₇H₂₁CoN₃O₂F₃·0.5H₂O·0.5C₅H₅N, space group *P2₁/c*, *a* = 14.255 (8) Å, *b* = 19.318 (8) Å, *c* = 19.434 (8) Å, *β* = 93.7 (1)°, *D*_{calcd} = 1.45 g cm⁻³, *Z* = 8, *R* = 0.055 for 13588 measured reflections. Several interesting features emerge from these structures. First, the Co atom in I and II is displaced toward R. Second, the Co-C bond is shorter than in hexacoordinate compounds, but steric strain remains for *i*-C₃H₇ even in the pentacoordinate species. Third, in the unusual example of both a dimeric and monomeric molecule in the same crystal in compound II, the monomeric form seems to be stabilized by the water of crystallization. This water is hydrogen-bonded to the saloph ligand and not coordinated to Co. Dynamic ¹H NMR measurements of 3,5-lut exchange in 3,5-lutCo(saloph)R (where 3,5-lut = 3,5-lutidine, R = CH₂CN, CH₂CF₃, or CH₃) reveal that the rate of exchange increases more rapidly with increasing electron donation by R in the series CH₂CN to CH₂CF₃ to CH₃ than in other classes of B₁₂ compounds. The saloph ligand has recently been shown to exhibit a large structural cis influence and a large kinetic cis effect compared to the other classes of models. It was also recently recognized that the trans and cis influences are synergistic. Thus, the dynamic NMR measurements provide evidence that the cis and trans kinetic effects are also synergistic. When R = CH₃, for example, exchange of the neutral axial ligand in saloph complexes is approximately 8 × 10¹⁰ times greater than in comparable cobaloxime complexes, where the cis effect is small. The comparable ratio for the less electron-donating CH₂CN ligand is about 0.5 × 10¹⁰. Ligand-exchange reactions proceed through five-coordinate intermediates, and the implications of these results to the existence of stable five-coordinate cobalamins and cobaloximes in aqueous solution are discussed. Finally, the role of coordination number of coenzyme B₁₂ in B₁₂-dependent enzymic processes is considered.

Introduction

Although low-spin d⁶ Co(III) complexes ordinarily are hexacoordinate (octahedral or pseudooctahedral), pentacoordinate organocobalt(III) species have been suspected to exist either as reactive intermediates in ligand-exchange reactions¹⁻¹¹ or, less commonly, as relatively stable species.^{7,12-14} Clear-cut demonstrations of stable five-coordinate Co(III) complexes are relatively rare,¹⁵ but suggestive evidence for such species has been presented

for a range of organocobalt(III) B₁₂ models as well as for cobalamins.¹²

The types of model systems in which five-coordinate species have been invoked range from the relatively "electron-deficient" cobaloximes to the relatively "electron-rich" Schiff base complexes, where the corrin ring in cobalamins is replaced by two dioximate ligands or by a tetradentate N₂O₂ dinegative Schiff base ligand, respectively. These two classes of models, in fact, appear to "bracket" many characteristics of cobalamins since the cobaloximes are too electron-deficient and the Schiff base complexes are too electron-rich.^{2,13,14,16} As such, an understanding of the differences in properties between these two types of systems could provide useful insight into the chemistry and biochemistry of cobalamins.

Indeed, Halpern and co-workers¹⁷⁻²⁰ have been able to estimate the Co-C bond energies in two series of complexes which are members of the two classes of complexes. The specific complexes studied were the cobaloximes of the type LCo(DH)₂CH(C-

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$H_3)(C_6H_5)$ (where L = neutral O, N, or P donor and DH = monoanion of dimethylglyoxime) and the Schiff base complexes of the type $pyCo(saloph)R$ (where py = pyridine, saloph = dianion of disalicylidene-*o*-phenylenediamine, and R = alkyl ligands of varying bulk). These studies have been recently reviewed.²⁰⁻²² Recent ligand-exchange and structural data,²³ together with estimates of the Co-C homolysis rate,¹⁸ support the notion that the $Co(saloph)$ model system contains a Co center which reproduces the Co center in cobalamins better than do most other models.¹⁸ Although a Schiff base system, the saloph system more closely reflects the properties of cobalamins than do other related systems (such as the salen (dianion of disalicylideneethylenediamine compounds)) which lack the electron-withdrawing phenylene ring. Thus, we have been able to characterize two six-coordinate organometallic complexes in this series.²³

Another type of model deserves mentioning. This is the mixed Schiff base/oxime system initially introduced by Costa and co-workers.¹³ The equatorial ligand employed here is the mononegative (DO)(DOH)pn (diacetyl-monoximeimino diacetylmonoximateiminopropane). Using a slightly modified version of this equatorial ligand system, Finke and co-workers were able to demonstrate that the Co center has some properties similar to cobalamins;²⁴ in particular it is a ± 0.5 -V mimic of the Co(III)/Co(II) and base-off Co(II)/Co(I) $E_{1/2}$ values. This system also appears to facilitate rearrangement reactions similar to those in enzymic processes better than other models.²⁵ More work is needed on both the Costa model and on the saloph complexes in order to more fully evaluate organocobalt chemistry relevant to B_{12} biochemistry. Since the involvement of Co in the rearrangement reactions appears unlikely,^{20,25} we are concentrating our efforts on understanding the dynamic, thermodynamic, and structural features of both models and cobalamins as these may relate to the essential Co-C bond homolysis process in B_{12} -dependent enzyme-catalyzed reactions.²⁶

The suspected five-coordinate complexes, $Co(saloph)R$ and "base-off" alkylcobalamins, share the behavior that Co-C bond homolysis is less facile than in the counterpart six-coordinate complexes, $LCo(saloph)R$ and "base-on" alkylcobalamins.^{12,18,27} "Base-off" cobalamins (made by adding acid to protonate the benzimidazole ring) and cobinamides (which are derived from cobalamins but lack 5,6-dimethylbenzimidazole) are believed to be five-coordinate when R is a strong electron donor, but the evidence is primarily spectroscopic.^{12,28} For example, the six-coordinate forms are red, whereas a yellow color (440-nm absorption) has been interpreted to indicate a five-coordinate species.²⁹ Indeed, an ~ 440 -nm absorption has been observed during B_{12} -dependent enzymic processes, and it has been suggested that such five-coordinate species are relevant to the mechanism of action of B_{12} -dependent enzymes.²⁹ However, five-coordinate species generally are more thermally stable than their six-coordinate counterparts.

As mentioned above, the literature contains one clearly established five-coordinate organocobalt B_{12} model compound, namely $Co(acacen)CH_3$ (where acacen = dianion of bis(acetylacetone)-ethylenediimine).¹⁵ This system is one of the most electron-rich types of models.^{2,13,14} Complexes of the type $Co(\text{equatorial ligand})R$ have been frequently isolated, but these may be dimers.^{7,8,13,14} For example, $Co(DH)_2CH_3$ exists as a dimer

both in the solid and in solution.^{30,31} Complexes of the type $Co(saloph)R$ or $Co(saloph)R \cdot H_2O$ were known^{13,14} and, as mentioned above, this system reflects closely some properties of cobalamins. Therefore, we have investigated the structures of $Co(saloph)-i-C_3H_7 \cdot 1.5H_2O$ (compound I) and $Co(saloph)CH_3 \cdot 0.5H_2O$ (compound II). The *i*- C_3H_7 compound permits an assessment of the possible role of steric factors in stabilizing Co-C bonds to thermolysis. In addition, since we are also interested in exploring the dynamic properties of organocobalt complexes, for which compounds I and II would be intermediates, we have extended our studies of ligand exchange of $LCo(saloph)R$ complexes²³ by determining the dependence on R of the L ligand-exchange reaction. We now find that a parallel exists between the recently recognized enhanced structural cis influence when R is a good trans influence ligand²³ and an enhanced kinetic cis effect when R is a good trans effect ligand. Finally, we have obtained structural data on a third example of six-coordinate $pyCo(saloph)R$ complexes, namely, that with R = CH_2CF_3 . This compound, III, conforms with earlier trends and is described only briefly.

Experimental Section

Reagents. CD_2Cl_2 (99.8% D) was from MSD Isotopes. All other reagents were from Aldrich and were used without further purification, except for 3,5-lutidine (3,5-lut) which was distilled under vacuum.

¹H NMR Measurements. All ¹H NMR measurements were made with an IBM WP-200SY NMR spectrometer (200.13 MHz), equipped with a B-VT.1000 variable temperature unit which maintained the sample within ± 0.5 °C. NMR spectra were obtained with 0.05 M 3,5-lut- $Co(saloph)R$ solutions (CD_2Cl_2 , with added 3,5-lut (~ 0.05 M)) and the acquisition parameters reported previously.²³

¹H NMR Line-Shape Analyses. Dynamic ¹H NMR line shapes were simulated with the Nicolet program NMRXC. Rate constants were determined by varying τ (the exchange constant) until the experimental and computer-simulated line shapes were visually identical. For further information, see ref 23.

Rate Measurements. The rate of substitution of 3,5-lut in 3,5-lut- $Co(DH)_2R$ (R = CH_3 and CH_2CF_3) by $(CH_3O)_3P$ was determined spectrophotometrically with a Perkin-Elmer LAMBDA 3B instrument equipped with a Perkin-Elmer C570-0701 digital temperature controller. The data were analyzed as previously described⁶ and yield classical S_N1 LIM behavior.

Preparations. All saloph compounds were prepared in the dark as described previously.²³ X-ray quality crystals of III were obtained by dissolving the compound in pyridine (py) (0.3 g in 30 mL) and adding water (~ 5 mL) until the solution was slightly turbid. Crystals were obtained in 1 day at ambient *T*.

X-ray quality crystals of I and II were obtained by dissolving the compounds in acetone (0.3 g in 35 mL), adding water (~ 5 mL), and allowing the acetone to evaporate slowly in the dark at -5 °C. Crystals were obtained in 3-5 days.

3,5-lut- $Co(DH)_2R$ complexes were prepared by standard methods.⁶

Elemental analyses were obtained for the compounds employed in the rate studies (Atlantic Microlabs): 3,5-lut- $Co(saloph)CH_2CF_3$. Anal. Calcd for $C_{29}H_{25}CoN_3O_2F_3$: C, 61.82; H, 4.47; N, 7.46. Found: C, 61.68; H, 4.50; N, 7.45. 3,5-lut- $Co(saloph)CH_3 \cdot 1/4 H_2O$. Anal. Calcd for $C_{28}H_{26}CoN_3O_2 \cdot 1/4 H_2O$: C, 67.26; H, 5.34; N, 8.40. Found: C, 67.53; H, 5.72; N, 7.97; 3,5-lut- $Co(DH)_2CH_3 \cdot 1/2 H_2O$. Anal. Calcd for $C_{16}H_{26}CoN_3O_4 \cdot 1/2 H_2O$: C, 45.72; H, 6.47; N, 16.66. Found: C, 45.87; H, 6.35; N, 16.72. 3,5-lut- $Co(DH)_2CH_2CF_3$. Anal. Calcd for $C_{17}H_{25}CoN_3O_4F_3$: C, 42.60; H, 5.26; N, 14.61. Found: C, 42.45; H, 5.29; N, 14.57.

Crystal Data. Cell dimensions of crystals of the three compounds were determined 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 recording. Cell dimension, refinement, and data collection for I and III were carried out on a CAD-4 diffractometer and for II on a Siemens diffractometer.

Solution and Refinement of Structures. The structure of the three compounds were solved by conventional Patterson and Fourier methods and refined, excluding the carbon atoms, by the full-matrix anisotropic least-squares methods for III. Full-matrix anisotropic refinement for I

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Table I. Crystal Data for Compounds I-III

	I	II	III
form	$C_{23}H_{21}CoN_2O_2 \cdot 1.5H_2O$	$C_{21}H_{17}CoN_2O_2 \cdot 0.5H_2O$	$C_{27}H_{21}CoN_3O_2F_3 \cdot 0.5H_2O \cdot 0.5C_5H_5N$
M_r	443.4	397.3	584.0
a , Å	26.075 (6)	12.100 (8)	14.255 (8)
b , Å	9.617 (3)	20.392 (9)	19.318 (8)
c , Å	16.109 (3)	11.606 (8)	19.434 (8)
α , deg		53.3 (1)	
β , deg		127.6 (1)	93.7 (1)
γ , deg		121.7 (1)	
D_{meas} , g cm ⁻³	1.44	1.48	1.45
D_{calcd} , g cm ⁻³	1.46	1.50	1.45
Z	8	4	8
space gp	<i>Pbcn</i>	$P\bar{1}$	$P2_1/c$
μ , cm ⁻¹	9.1	10.4	7.2
cryst dims, cm ³	$0.04 \times 0.04 \times 0.06$	$0.03 \times 0.03 \times 0.06$	$0.04 \times 0.04 \times 0.05$
no. of reflects measd	5437	7360	13588
no. of independ. reflects	1898	2812	2833
($I \geq 3\sigma(I)$) max 2θ , deg (Mo K α)	28	27	27
R_w	0.078	0.055	0.064
R	0.057	0.041	0.055

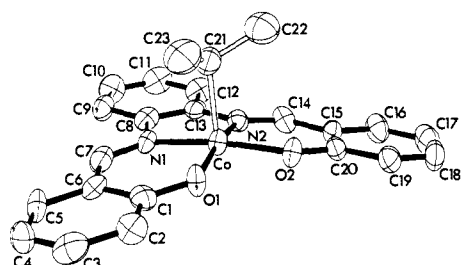


Figure 1. Shelxtl drawing with atom numbering scheme for I.

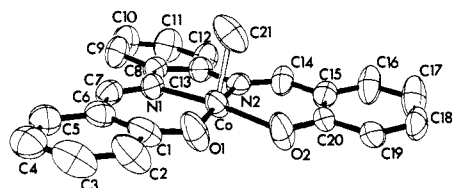


Figure 2. Shelxtl drawing with atom numbering scheme for IIB.

was performed. A block-diagonal refinement using anisotropic temperature factors for cobalt atoms and for the nonheavy atoms of only one of the two crystallographically independent molecules was carried out for II. The contribution of hydrogen atoms at calculated positions was held constant ($B = 5 \text{ \AA}^2$) in all the structures. In the final refinement, the weighting scheme was $w = 1/(\text{sig } F + (AF)^2 + B)$ where $A = 0.02$ (I), 0.025 (II), and 0.02 (III) and $B = 2.0$ (I), 5.7 (II), and 2.2 (III) were chosen so as to maintain $w(|F_o| - |F_c|)^2$ essentially constant over all ranges of $|F_o|$ and $\sin \theta/\lambda$. Atomic scattering factors utilized are given in ref 32. Final non-hydrogen positional parameters and relative B or B_{eq} factors are given in Tables II-IV. Hydrogen atom coordinates, anisotropic thermal parameters, and a list of final calculated and observed structure factors are given in the supplementary material. All calculations were done by using the computer programs from the SDP package.

Results

Structural Studies. ORTEP drawings of I, II, and III with the atom numbering scheme are depicted in Figures 1-3. For II and III, the numbering scheme refers to only one of the two crystallographically independent molecules. Selected bond lengths and angles are reported in Tables V, VI, and VII for compounds I, II, and III, respectively.

Dynamic NMR Studies. Activation parameters and extrapolated rate constants (25 °C) for the dissociation of 3,5-lut from 3,5-lutCo(saloph)R complexes with $R \approx CH_2CN$, CH_2CF_3 , and CH_3 are given in Table VIII. Values represent the mean \pm standard deviation for at least two sets of data. For a statistical treatment of the errors see ref 33. Previously,²³ the only comparison possible was with 4-CNpy (4-cyanopyridine) cobaloximes since CH_2CN is such a poor trans stabilizer.²² For $R = CH_2CF_3$ and CH_3 , the 3,5-lut dissociation rates could be determined for

Table II. Positional Parameters and Their Estimated Standard Deviations for Compound I

atom	x	y	z	$B(A^2)$
Co	0.094 35 (3)	0.1919 (1)	0.052 40 (7)	2.50 (2)
O1	0.105 3 (2)	0.3344 (5)	-0.024 7 (4)	3.0 (1)
O2	0.024 9 (2)	0.2408 (6)	0.039 9 (4)	3.0 (1)
N1	0.162 8 (2)	0.1311 (7)	0.050 1 (5)	2.5 (1)
N2	0.081 1 (2)	0.0269 (7)	0.110 8 (4)	2.6 (1)
C1	0.147 7 (3)	0.3725 (8)	-0.060 5 (6)	2.9 (2)
C2	0.147 8 (3)	0.487 (1)	-0.114 2 (6)	3.5 (2)
C3	0.192 6 (4)	0.5295 (9)	-0.151 9 (6)	4.0 (2)
C4	0.238 9 (3)	0.461 (1)	-0.139 1 (6)	3.9 (2)
C5	0.240 0 (3)	0.352 (1)	-0.085 6 (6)	3.7 (2)
C6	0.195 6 (3)	0.3030 (9)	-0.046 2 (5)	2.9 (1)
C7	0.199 9 (3)	0.188 (1)	0.008 3 (6)	3.3 (2)
C8	0.171 3 (3)	0.0136 (8)	0.102 5 (6)	2.9 (2)
C9	0.219 0 (3)	-0.045 (1)	0.121 0 (6)	3.4 (2)
C10	0.220 6 (4)	-0.1601 (9)	0.171 7 (7)	4.3 (2)
C11	0.176 9 (4)	-0.2179 (9)	0.204 7 (6)	4.2 (2)
C12	0.129 1 (4)	-0.1616 (9)	0.184 7 (6)	3.9 (2)
C13	0.126 7 (3)	-0.0466 (9)	0.134 6 (5)	2.7 (2)
C14	0.036 4 (3)	-0.0256 (8)	0.126 4 (6)	3.2 (2)
C15	-0.011 4 (3)	0.0390 (9)	0.106 2 (5)	3.0 (2)
C16	-0.056 6 (3)	-0.032 (1)	0.128 2 (7)	3.9 (2)
C17	-0.104 4 (3)	0.022 (1)	0.109 4 (7)	4.6 (2)
C18	-0.107 2 (3)	0.149 (1)	0.068 5 (6)	4.4 (2)
C19	-0.064 0 (3)	0.2212 (9)	0.046 8 (6)	3.6 (2)
C20	-0.015 1 (3)	0.1677 (8)	0.062 6 (5)	2.8 (2)
C21	0.107 6 (3)	0.298 (1)	0.159 3 (6)	3.5 (2)
C22	0.062 8 (4)	0.295 (1)	0.216 3 (7)	5.2 (3)
C23	0.125 3 (5)	0.442 (1)	0.137 5 (7)	5.6 (3)
OW1	0.009 5 (3)	0.4502 (9)	-0.097 8 (5)	6.9 (2)
OW2	0.000	0.312 (1)	-0.250	8.0 (4)

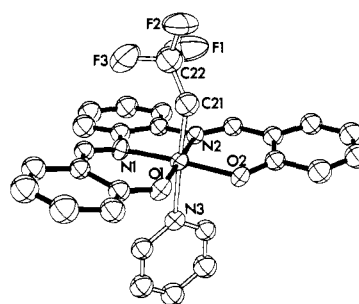


Figure 3. Shelxtl drawing with atom numbering scheme for IIIB. The atom numbering scheme for the equatorial ligand is the same as that in I and IIB.

cobaloximes and are $1.37 \pm 0.08 \times 10^{-5}$ and $3.37 \pm 0.02 \times 10^{-3} \text{ s}^{-1}$.

Description of the Structures. **Co(saloph)-*i*-C₃H₇.** The crystals of I are composed of Co(saloph)-*i*-C₃H₇ units held together by

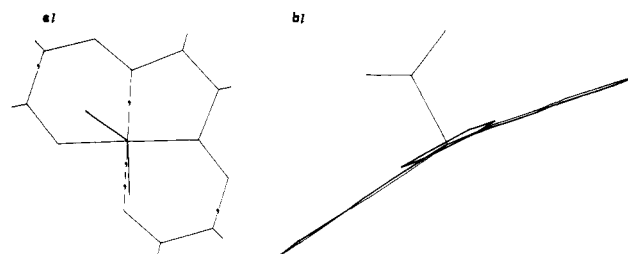
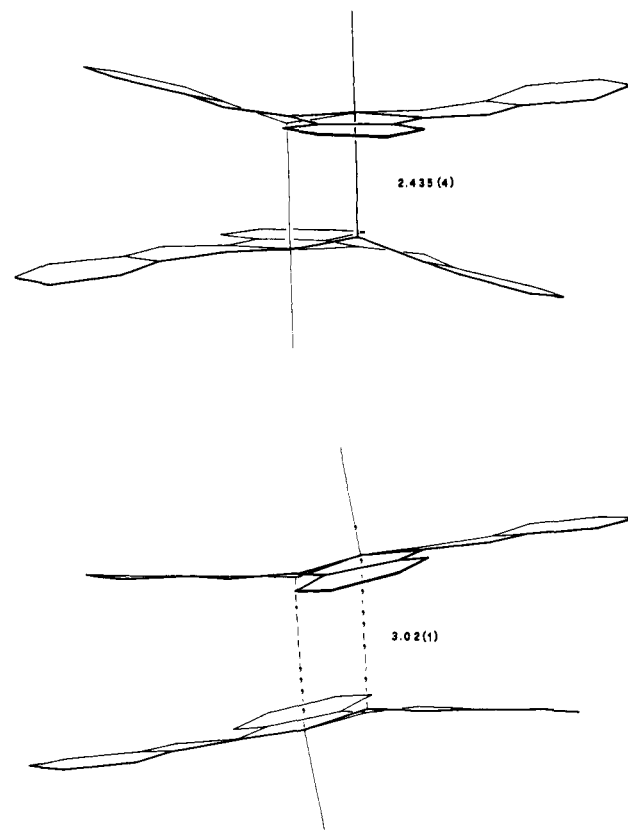
Table III. Positional Parameters ($\times 10^4$) and Their Estimated Standard Deviations for Compound II^a

	x	y	z	B
Co(1)	5889 (11)	232 (0)	-862 (1)	2.15 (9)
O(1)	5736 (4)	909 (2)	-354 (4)	2.7 (1)*
O(2)	4312 (4)	593 (2)	-2818 (4)	2.9 (1)*
N(1)	7462 (4)	-118 (2)	1121 (4)	2.3 (1)*
N(2)	5885 (4)	-554 (2)	-1211 (5)	2.4 (1)*
C(1)	6838 (5)	1278 (3)	621 (5)	2.4 (1)*
C(2)	6754 (6)	1990 (3)	484 (6)	3.0 (2)*
C(3)	7846 (6)	2356 (4)	1563 (7)	3.7 (2)*
C(4)	9040 (6)	2031 (4)	2809 (7)	3.7 (2)*
C(5)	9171 (6)	1343 (3)	2966 (66)	3.1 (2)*
C(6)	8090 (5)	964 (3)	1865 (6)	2.6 (1)*
C(7)	8277 (5)	242 (3)	2112 (6)	2.8 (2)*
C(8)	7798 (5)	-785 (3)	1392 (6)	2.5 (1)*
C(9)	8900 (6)	-1177 (3)	2753 (6)	3.2 (2)*
C(10)	9129 (6)	-1808 (4)	2837 (7)	3.9 (3)*
C(11)	8271 (6)	-2047 (4)	1576 (7)	3.9 (3)*
C(12)	7170 (6)	-1665 (4)	214 (7)	3.4 (2)*
C(13)	6938 (5)	-1029 (3)	119 (6)	2.5 (2)*
C(14)	5013 (5)	-707 (3)	-2499 (6)	2.9 (2)*
C(15)	3967 (6)	-242 (3)	-3898 (6)	3.0 (2)*
C(16)	3194 (6)	-434 (4)	-5252 (7)	3.5 (2)*
C(17)	2231 (7)	24 (4)	-6685 (7)	4.0 (3)*
C(18)	2015 (7)	673 (4)	-6809 (7)	4.0 (3)*
C(19)	2723 (6)	865 (4)	-5513 (7)	3.6 (2)*
C(20)	3721 (5)	402 (3)	-4009 (6)	2.8 (2)*
C(21)	7227 (6)	1135 (4)	-1813 (7)	3.6 (2)*
O(3)	5726 (8)	2391 (4)	3214 (9)	9.5 (5)
Co(2)	5613 (1)	4656 (1)	-607 (1)	4.7 (1)
O(91)	4347 (6)	3938 (4)	362 (6)	9.3 (3)
O(92)	6996 (5)	4161 (3)	1417 (5)	6.5 (3)
N(91)	4199 (5)	5186 (3)	-2557 (6)	3.9 (2)
N(92)	6925 (5)	5486 (3)	-1466 (6)	3.7 (2)
C(91)	2937 (7)	3730 (4)	-383 (9)	5.3 (3)
C(92)	2181 (9)	3018 (5)	547 (9)	6.0 (4)
C(93)	709 (9)	2782 (4)	-156 (11)	6.3 (4)
C(94)	-79 (9)	3211 (4)	-1767 (13)	7.3 (4)
C(95)	629 (8)	3916 (4)	-2685 (11)	6.1 (3)
C(96)	2141 (7)	4172 (4)	-1998 (8)	4.7 (3)
C(97)	2820 (7)	4917 (4)	-2998 (9)	4.6 (3)
C(98)	4784 (7)	5913 (4)	-3639 (7)	4.1 (3)
C(99)	4016 (8)	6472 (4)	-5127 (9)	5.4 (4)
C(910)	4720 (9)	7157 (5)	-6074 (10)	6.5 (4)
C(911)	6170 (9)	7278 (4)	-5530 (9)	6.2 (4)
C(912)	6940 (8)	6734 (4)	-4054 (8)	5.1 (3)
C(913)	6256 (7)	6065 (3)	-3065 (7)	3.8 (3)
C(914)	8301 (7)	5593 (4)	-719 (8)	4.2 (3)
C(915)	9079 (7)	5070 (4)	894 (8)	4.3 (3)
C(916)	10604 (8)	5287 (4)	1528 (8)	5.1 (3)
C(917)	11456 (8)	4812 (5)	3086 (9)	5.6 (4)
C(918)	10716 (9)	4097 (5)	3995 (9)	6.5 (4)
C(919)	9260 (9)	3875 (5)	3430 (9)	6.5 (4)
C(920)	8377 (8)	4367 (4)	1860 (7)	5.0 (4)
C(921)	5235 (8)	3891 (4)	-1368 (10)	6.3 (4)

^aStarred atoms were refined isotropically.

van der Waals interactions and through weak hydrogen bonds (O(1) (2.977 (8) Å) and O(2) (3.023 (9) Å)) to a water molecule (OW1). OW1 also makes a shorter hydrogen bond (2.801 (9) Å) with a second water molecule OW2.

The cobalt atom is five-coordinate, with a distorted square-pyramidal stereochemistry. The atoms of the N_2O_2 basal set are coplanar within ± 0.03 Å, and the cobalt is displaced by 0.16 Å above this mean plane toward the apical *i*-C₃H₇ group. The Co-C bond length is only 2.031 (8) Å, whereas the bond lengths and angles in the Co(saloph) moiety are quite normal (Table V). The *i*-C₃H₇ group is oriented with respect to the equatorial coordination plane in such a way that its methyl groups lie nearly above O(1) and O(2). As a consequence, the O-Co-C(21) angles (mean 98.6°) are larger than the N-Co-C(21) angles (mean 91.3°). The Co(saloph) unit is significantly distorted from planarity with an umbrella-shaped conformation and an α value of -15.0° , away from the *i*-C₃H₇ ligand, while the phenylene bridging group is slightly bent toward the apical group (Figure 4). The other interplanar angles of interest are given in Table IX.

**Figure 4.** View of I along the perpendicular to the O₂N₂ equatorial plane (a); a side view of I (b).**Figure 5.** Side view of the molecules A and B of II together with their centrosymmetric counterpart.

Co(saloph)CH₃. There are two crystallographically independent molecules of II which are arranged differently around the crystallographic nonequivalent centers. Molecules of A form dimeric units, [Co(saloph)CH₃]₂. The O(1)' atom of one [Co(saloph)CH₃] unit coordinates to Co of the other unit and both Co's are six-coordinate. The units are related by a symmetry center. The Co-O(1)' distance is 2.435 (4) Å. Formation of the dimeric species in the solid state has been observed for other Schiff base complexes, such as [Co(salen)CH₂CH₃]₂.³⁴ On the contrary, the arrangement of molecule B around the symmetry center does not permit dimer formation, and the Co-O(91)' distance is 3.02 (1) Å. The main differences between the two types of molecules are shown in Figure 5. A side view and the view along the perpendicular to the coordination plane of both molecules A and B and their centrosymmetric counterpart are compared. Formation of dimeric units for molecule A is confirmed by the difference between the Co-O(1) distance (1.914 (6) Å) and the Co-O(2) distance (1.877 (3) Å) which is indicative of additional coordination by O(1). In contrast, no difference is detected for the Co-O

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Table IV. Positional Parameters and Their Estimated Standard Deviations for Compound III^a

molecule A					molecule B				
atom	x	y	z	B(A ²)	atom	x	y	z	B(A ²)
Co1	-0.025 86 (9)	0.197 09 (8)	0.193 02 (7)	2.49 (3)	Co2	0.4869 (1)	0.206 36 (8)	0.052 68 (7)	2.67 (3)
F1	0.116 5 (7)	0.054 2 (5)	0.162 3 (5)	8.3 (2)	F91	0.4131 (6)	0.058 2 (4)	0.201 6 (4)	6.6 (2)
F2	0.150 8 (6)	0.131 9 (5)	0.096 1 (6)	9.4 (3)	F92	0.5242 (6)	0.132 5 (4)	0.216 3 (4)	6.5 (2)
F3	0.070 5 (6)	0.046 0 (4)	0.056 0 (4)	6.7 (2)	F93	0.5305 (5)	0.054 6 (4)	0.139 0 (4)	5.5 (2)
O1	-0.104 1 (5)	0.247 1 (3)	0.127 5 (4)	2.8 (2)	O91	0.3652 (5)	0.228 8 (4)	0.015 1 (4)	3.5 (2)
O2	-0.139 0 (5)	0.150 8 (4)	0.213 6 (4)	3.1 (2)	O92	0.4701 (5)	0.281 4 (4)	0.113 7 (4)	3.4 (2)
N1	0.085 9 (6)	0.244 5 (4)	0.174 4 (4)	2.8 (2)	N91	0.5021 (6)	0.131 8 (5)	-0.007 2 (4)	2.7 (2)
N2	0.050 0 (6)	0.149 5 (4)	0.260 8 (5)	2.8 (2)	N92	0.6127 (6)	0.188 2 (4)	0.086 5 (4)	2.8 (2)
N3	-0.053 9 (6)	0.274 0 (4)	0.267 5 (4)	2.8 (2)	N93	0.5417 (6)	0.275 5 (5)	-0.019 4 (5)	3.4 (2)
C1	-0.073 6 (8)	0.286 1 (6)	0.079 3 (5)	3.1 (2)*	C91	0.3133 (8)	0.189 0 (6)	-0.028 5 (6)	3.3 (2)*
C2	-0.142 8 (9)	0.311 2 (7)	0.028 0 (6)	4.2 (3)*	C92	0.2183 (9)	0.212 8 (7)	-0.044 2 (7)	4.7 (3)*
C3	-0.114 4 (9)	0.355 1 (7)	-0.023 0 (7)	4.5 (3)*	C93	0.163 (1)	0.174 1 (8)	-0.090 9 (8)	5.8 (3)*
C4	-0.022 5 (9)	0.376 4 (7)	-0.025 2 (7)	4.5 (3)*	C94	0.193 (1)	0.114 7 (8)	-0.121 4 (8)	5.9 (3)*
C5	0.045 8 (8)	0.352 2 (6)	0.021 1 (6)	3.8 (3)*	C95	0.282 (1)	0.093 2 (7)	-0.105 4 (7)	5.1 (3)*
C6	0.021 5 (7)	0.306 6 (6)	0.074 8 (5)	3.1 (2)*	C96	0.3444 (8)	0.130 5 (6)	-0.059 7 (6)	3.5 (2)*
C7	0.094 8 (7)	0.285 3 (6)	0.124 2 (5)	3.0 (2)*	C97	0.4381 (8)	0.104 4 (6)	-0.048 5 (6)	3.3 (2)*
C8	0.160 4 (8)	0.228 5 (6)	0.223 9 (5)	2.9 (2)*	C98	0.5961 (7)	0.104 5 (6)	-0.003 0 (5)	2.8 (2)*
C9	0.248 6 (8)	0.261 3 (6)	0.227 2 (6)	3.8 (2)*	C99	0.6305 (8)	0.051 8 (6)	-0.042 8 (6)	3.6 (2)*
C10	0.316 7 (9)	0.240 6 (7)	0.278 1 (7)	4.6 (3)*	C910	0.7199 (9)	0.029 8 (6)	-0.032 3 (6)	3.8 (3)*
C11	0.296 6 (9)	0.190 5 (7)	0.323 6 (7)	4.8 (3)*	C911	0.7810 (8)	0.061 4 (6)	0.017 0 (6)	3.5 (2)*
C12	0.209 7 (9)	0.158 0 (7)	0.321 1 (7)	4.5 (3)*	C912	0.7491 (8)	0.113 6 (6)	0.058 4 (6)	3.5 (2)*
C13	0.142 0 (8)	0.176 5 (6)	0.268 2 (6)	3.1 (2)*	C913	0.6557 (7)	0.135 9 (5)	0.047 7 (5)	2.7 (2)*
C14	0.025 5 (7)	0.094 5 (6)	0.292 4 (5)	2.9 (2)*	C914	0.6575 (8)	0.219 5 (6)	0.137 3 (6)	3.1 (2)*
C15	-0.066 0 (7)	0.063 6 (6)	0.287 7 (5)	2.9 (2)*	C915	0.6200 (8)	0.272 3 (6)	0.179 9 (6)	3.0 (2)*
C16	-0.080 8 (9)	0.002 2 (6)	0.324 8 (6)	3.8 (2)*	C916	0.6769 (8)	0.297 3 (7)	0.236 0 (6)	3.7 (2)*
C17	-0.167 5 (9)	-0.027 9 (7)	0.324 2 (7)	4.7 (3)*	C917	0.6425 (9)	0.348 0 (7)	0.279 7 (7)	4.6 (3)*
C18	-0.241 3 (9)	0.000 2 (7)	0.285 8 (7)	4.9 (3)*	C918	0.5542 (9)	0.372 9 (7)	0.264 9 (7)	4.6 (3)*
C19	-0.231 8 (8)	0.060 9 (6)	0.248 5 (6)	3.8 (2)*	C919	0.4986 (8)	0.351 9 (6)	0.210 5 (6)	3.6 (2)*
C20	-0.144 0 (7)	0.094 7 (6)	0.249 9 (6)	3.0 (2)*	C920	0.5273 (7)	0.299 9 (6)	0.165 1 (5)	2.8 (2)*
C21	-0.007 5 (8)	0.127 0 (6)	0.121 4 (6)	3.9 (3)*	C921	0.4244 (9)	0.143 7 (6)	0.117 8 (6)	4.1 (3)*
C22	0.080 3 (9)	0.089 8 (7)	0.110 0 (7)	4.8 (3)*	C922	0.4721 (9)	0.099 7 (7)	0.165 5 (7)	4.2 (3)*
C23	-0.086 9 (8)	0.257 2 (6)	0.327 6 (6)	3.6 (2)*	C923	0.536 (1)	0.264 2 (8)	-0.086 6 (8)	6.1 (4)*
C24	-0.109 2 (8)	0.307 6 (7)	0.374 0 (6)	4.3 (3)*	C924	0.567 (1)	0.307 1 (9)	-0.135 4 (9)	7.5 (4)*
C25	-0.097 8 (9)	0.376 1 (7)	0.360 1 (7)	4.6 (3)*	C925	0.610 (1)	0.366 1 (8)	-0.112 5 (8)	5.9 (3)*
C26	-0.064 0 (9)	0.393 1 (7)	0.298 2 (7)	4.6 (3)*	C926	0.616 (1)	0.382 9 (9)	-0.046 1 (8)	6.9 (4)*
C27	-0.044 1 (8)	0.340 1 (6)	0.252 6 (6)	3.6 (2)*	C927	0.582 (1)	0.334 2 (8)	0.000 2 (7)	5.7 (3)*
O3	0.298 2 (6)	0.361 8 (5)	0.088 5 (5)	6.8 (3)					
N4	0.719 5 (9)	0.545 7 (7)	0.029 5 (7)	7.0 (3)*					
C30	0.643 (1)	0.548 (1)	0.063 (1)	9.6 (6)*					
C31	0.636 (2)	0.507 (1)	0.119 (1)	10.6 (6)*					
C32	0.704 (1)	0.467 (1)	0.139 (1)	9.9 (6)*					
C33	0.788 (1)	0.465 (1)	0.107 (1)	8.8 (5)*					
C34	0.788 (1)	0.505 2 (9)	0.049 3 (9)	6.9 (4)*					

^a Starred atoms were refined isotropically.

Table V. Selected Bond Distances (Å) and Bond Angles (deg) for Compound I

Co-O(1)	1.872 (5)	O(1)-Co-O(2)	83.9 (2)
Co-O(2)	1.883 (4)	O(1)-Co-N(1)	94.0 (2)
Co-N(1)	1.879 (5)	O(1)-Co-N(2)	168.5 (2)
Co-N(2)	1.877 (6)	O(1)-Co-C(21)	99.7 (3)
Co-C(21)	2.031 (8)	O(2)-Co-N(1)	171.9 (3)
		O(2)-Co-N(2)	95.0 (2)
		O(2)-Co-C(21)	97.4 (3)
		N(1)-Co-N(2)	85.5 (2)
		N(1)-Co-C(21)	90.7 (3)
		N(2)-Co-C(21)	91.8 (3)

distances of molecule B. Furthermore, the deformations of the Co(saloph) moiety of A, which are significantly larger than those

Table VI. Selected Bond Distances (Å) and Bond Angles (deg) for Compounds IIA and IIB

	molec A	molec B		molec A	molec B
Co-O(1)	1.914 (6)	1.879 (7)	C(21)-Co-O(1)	95.7 (3)	96.3 (4)
Co-O(2)	1.877 (3)	1.865 (4)	C(21)-Co-O(2)	90.6 (2)	93.7 (3)
Co-N(1)	1.882 (3)	1.872 (4)	C(21)-Co-N(1)	89.9 (2)	91.0 (3)
Co-N(2)	1.870 (7)	1.863 (6)	C(21)-Co-N(2)	92.1 (3)	92.6 (4)
Co-C(21)	1.963 (7)	1.957 (13)	O(1)-Co-O(1)	85.2 (2)	
Co-O(1)'	2.435 (4)		O(1)-Co-O(2)	90.5 (2)	
O(1)-Co-O(2)	85.2 (2)	84.4 (2)	O(1)-Co-N(1)	89.1 (1)	
O(1)-Co-N(1)	93.3 (2)	93.0 (3)	O(1)-Co-N(2)	87.1 (2)	
N(1)-Co-N(2)	86.0 (2)	86.6 (2)	O(1)-Co-C(21)	178.7 (3)	
O(2)-Co-N(2)	95.5 (2)	95.3 (2)			

of molecule B (Table IX) and the trend of the corresponding thermal B_{eq} factors are both consistent with the formation of dimers by A but not by B. Finally, small differences in the coordination geometry around Co(1) and Co(2) support this conclusion. The N₂O₂ equatorial donor atoms are coplanar within ± 0.06 Å in A and within ± 0.03 in B. The cobalt is displaced from this plane toward the CH₃ group by 0.07 Å in A and 0.11 Å in B. The formation of the dimer produces a minor displacement of Co toward the apical group and a larger displacement of O(1) out of the coordination plane toward the Co of the centrosymmetric unit, as shown by the side view of Figure 5.

The overall conformation of A may be described as an asymmetric "umbrella" with bending toward the apical CH₃ group, while for B it may be described as an asymmetric "step". In fact, it has been shown that for this kind of ligand, the umbrella shape

Table VII. Selected Bond Distances (Å) and Bond Angles (deg) for Compounds IIIA and IIIB

	molec A	molec B		molec A	molec B
Co-O(1)	1.900 (6)	1.894 (6)	N(3)-Co-O(2)	89.1 (3)	89.8 (3)
Co-O(2)	1.908 (6)	1.898 (7)	N(3)-Co-N(1)	89.5 (3)	90.7 (4)
Co-N(1)	1.892 (8)	1.870 (8)	N(3)-Co-N(2)	89.5 (3)	88.0 (3)
Co-N(2)	1.882 (8)	1.899 (7)	C(21)-Co-O(1)	88.5 (4)	87.0 (4)
Co-N(3)	2.127 (8)	2.121 (9)	C(21)-Co-O(2)	88.8 (4)	89.3 (4)
Co-C(21)	1.975 (11)	2.001 (11)	C(21)-Co-N(1)	92.7 (4)	90.2 (4)
C(21)-C(22)	1.46 (2)	1.398 (15)	C(21)-Co-N(2)	93.6 (4)	96.8 (4)
C(22)-F(1)	1.313 (13)	1.388 (13)	C(21)-Co-N(3)	176.3 (4)	175.1 (4)
C(22)-F(2)	1.338 (14)	1.356 (12)	Co-C(21)-C(22)	126.7 (8)	124.7 (9)
C(22)-F(3)	1.343 (13)	1.332 (13)	C(21)-C(22)-F(1)	116 (1)	114 (1)
O(1)-Co-O(2)	85.1 (3)	85.2 (3)	C(21)-C(22)-F(2)	113 (1)	115 (1)
O(1)-Co-N(1)	95.0 (3)	94.5 (3)	C(21)-C(22)-F(3)	113 (1)	116 (1)
N(1)-Co-N(2)	85.5 (3)	86.0 (3)	F(1)-C(22)-F(2)	101 (1)	102.7 (9)
N(2)-Co-O(2)	94.4 (3)	94.4 (3)	F(1)-C(22)-F(3)	107 (1)	103 (1)
N(3)-Co-O(1)	88.4 (3)	88.2 (3)	F(2)-C(22)-F(3)	105 (1)	105 (1)

Table VIII. Activation Parameters and Extrapolated Rate Constants (25 °C) for the Dissociation of 3,5-lut from 3,5-lutCo(saloph)R^a

R	E _a , kcal/mol	ln A	k(25 °C), s ⁻¹
CH ₂ CN ^b	18.2 ± 0.6	40.7 ± 1.2	2.25 ± 0.27 × 10 ⁴
CH ₂ CF ₃	20.2 ± 0.3	47.0 ± 0.4	4.35 ± 0.21 × 10 ⁵
CH ₃	20.1 ± 0.6	53.4 ± 0.9	2.75 ± 0.35 × 10 ⁸

^aCD₂Cl₂, from DNMR data. ^bFrom ref 23; CDCl₃.

Table IX. Interplanar Angles of Interest in I, II, and III

planes ^a	interplanar angles, deg ^b				
	I	II		III	
		mol A	mol B	mol A	mol B
1-2	-5.2	16.9	11.2	9.3	8.2
1-4	-10.1	4.5	-4.6	11.4	4.7
2-4	-15.3	18.8	7.6	20.7	12.8
1-3	3.9	-5.1	-6.7	-10.0	-5.9
1-5	-4.8	17.4	12.0	8.8	8.1
1-6	-10.2	7.1	-6.0	11.5	5.8
5-6	-15.0	21.0	7.9	20.2	13.8

^aPlanes are defined as follows: (1) O(1), O(2), N(1), N(2); (2) O(1), N(1), C(1), C(6), C(7); (3) C(8)-C(13); (4) O(2), N(2), C(14), C(15), C(20); (5) O(1), N(1), C(1)-C(7); (6) O(2), N(2), C(14)-C(20). ^bThe sign - refers to bending toward the axial pyridine group and the sign + toward toward the alkyl group.

conformation is characterized by the following relation between the angles given in Table IX: $|5^{\Delta}6| = |1^{\Delta}2| + |1^{\Delta}4|$, while for a step conformation the relation is $|1^{\Delta}2| = |5^{\Delta}6| + |1^{\Delta}4|$.³⁴

pyCo(saloph)CH₂CF₃. Crystals of III contain discrete pyCo(saloph)CH₂CF₃ molecules, two of which are crystallographically independent, A and B. One water molecule and one pyridine molecule of crystallization for each pair of pyCo(saloph)CH₂CF₃ units are held together by a N...H-OH bond (2.91 (1) Å) with the O(2) atom of the molecule B. The cobalt atoms exhibit distorted octahedral stereochemistry with the saloph ligand at the four equatorial positions. Respective bond lengths and angles in the two crystallographically independent molecules A and B are equal within experimental error. The Co(saloph) units deviate significantly from planarity. The cobalt atom is nearly in the plane of the N₂O₂ equatorial donors (which are coplanar within ±0.06 Å in molecule A and ±0.03 Å in molecule B) but is displaced by 0.03 Å in A and B toward the alkyl group. In both A and B, the two salicylaldehyde residues tilt toward CH₂CF₃. Thus, the Co(saloph) units assume an umbrella-shaped conformation with interplanar angles of 20.2° and 13.8° in A and B, respectively (Figure 6). The positive sign indicates a bending toward CH₂CF₃. On the other hand, the bridging phenylene ring bends toward the pyridine. The interplanar angles of interest are given in Table IX. The values of the interplanar angles are significantly smaller in molecule B because the two halves of the saloph ligand are twisted with respect to each other (Figure 6). The orientation of the CH₂CF₃ group with respect to the equatorial ligand is different in A and B (Figure 7), while the pyridine ligands in both A and B have a similar orientation lying over the six-membered

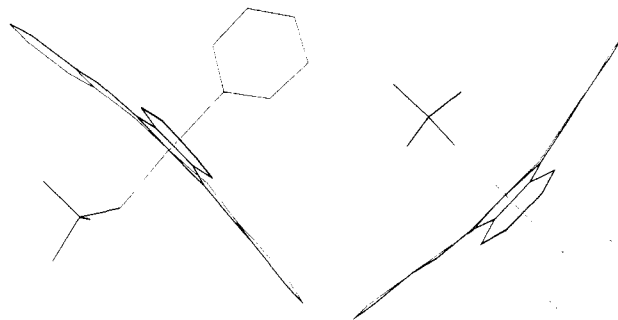
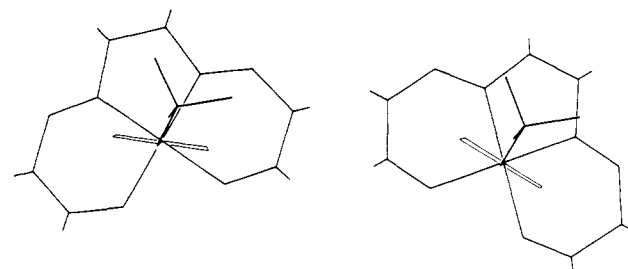


Figure 6. Side view of molecules A and B of III.

Figure 7. View of molecules A and B of III along a perpendicular to the O₂N₂ equatorial plane.

ribs of the equatorial ligand. The mean Co-C and Co-py bond lengths are 1.99 (1) and 2.124 (9) Å, respectively, with a mean py-Co-C angle of 175.7 (4)°. The steric interaction of the CH₂CF₃ group with the equatorial moiety provokes a noticeable widening of the Co-CH₂-CF₃ angle (mean value of 125.7 (9)°) as already observed³⁵ for analogous cobaloxime complexes. Furthermore, a compression of the CF₃ group is observed as shown by the values of the FCF angles which vary from 101(1)° to 107(1)°.

Structural Comparisons. The presence of monomeric and dimeric units in the same crystal of II may be attributed to the formation of a hydrogen bond between a water molecule and the O(1) atom of the molecule B. On the contrary, no hydrogen bond is formed with molecule A. The involvement of O(1) in hydrogen bonding should hinder dimer formation as suggested by the structural results for the compounds [Cu(salen)]₂ and Cu(salen)(solvent) where solvent = CHCl₃ or *p*-NO₂C₆H₄OH.³⁶ The green solvent-free crystals are built up by dimeric units with an axial Cu-O distance of 2.41 Å. The crystals containing CHCl₃ contain loosely held dimeric units, with a Cu-O distance of 2.79 Å, and a short distance (3.03 Å) between O and the C of CHCl₃.

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Table X. Comparison of the Geometry of the py-Co-Alkyl Fragment and the Dihedral Angle, α , between the Two Halves of the Equatorial Ligand in Some B₁₂ Models

	Co—C, Å	Co— N(py), Å	Co— CH ₂ —R, deg	α , deg
pyCo(acacen)CH ₃ ^a	1.99 (1)	2.16 (1)		7
pyCo(DH) ₂ CH ₃ ^b	1.998 (5)	2.068 (3)		3
pyCo(salen)CH=CH ₂ ^a	1.93 (2)	2.12 (1)		17
pyCo(DH) ₂ CH=CH ₂ ^b	1.966 (6)	2.073 (3)		6
pyCo(saloph)CH ₂ CH ₃ ^c	2.042 (6)	2.215 (4)	117.3 (5)	-25
4-CH ₃ OC(NH)pyCo- (DH) ₂ CH ₂ CH ₃ ^d	2.035 (5)	2.081 (5)	117.2 (4)	9
pyCo(saloph)CH ₂ CN ^e	1.999 (5)	2.098 (5)	114.2 (9)	18
pyCo(DH) ₂ CH ₂ NO ₂ ^e	2.002 (3)	2.028 (3)	113.2 (7)	0
pyCo(saloph)CH ₂ CF ₃ ^f	1.99 (1)	2.124 (9)	125.7 (9)	17
4-CNpyCo(DH) ₂ - CH ₂ CF ₃ ^g	2.010 (3)	2.041 (3)	122.6 (3)	-1

^aReferences 15 and 34. ^bBresciani-Pahor, N.; Calligaris, M.; Randaccio, L. *J. Organomet. Chem.* **1980**, *189*, C53. ^cReference 23. ^dMarzilli, L. G.; Summers, M. F.; Ramsden, J. H.; Bresciani-Pahor, N.; Randaccio, L. *J. Chem. Soc., Dalton Trans.* **1984**, 511. ^eRandaccio, L.; Bresciani-Pahor, N.; Toscano, P. J.; Marzilli, L. G. *Inorg. Chem.* **1981**, *20*, 2722. ^fPresent work. ^gReference 35; 4-CNpy = 4-cyanopyridine.

Finally, the violet crystals containing *p*-nitrophenol have monomeric Cu(salen) with a strong hydrogen bond (2.66 Å) involving the OH group of *p*-nitrophenol.

For II, the axial Co—CH₃ bond length of 1.963 (7) Å in A is similar to that of 1.957 (13) Å in molecule B and is not affected by dimer formation. The mean value of 1.960 (10) Å seems slightly smaller than those reported for hexacoordinate saloph complexes which range from 1.99 (1) to 2.042 (7) Å (Table X). On the contrary, the Co atom displacements out of the coordination plane toward the alkyl group, mentioned above, are significantly larger than the 0.02–0.03 Å found in pyCo(saloph)R.

In the monomeric compound Co(acacen)CH₃, the only other structurally pentacoordinate Co Schiff base organometallic complex, the Co—C distance is 1.952 (18) Å and the Co displacement is 0.11 Å.¹⁵ These values, although of lower accuracy, are in agreement with those found here for Co(saloph)CH₃.

The Co—C bond length in II appears significantly shorter than that of 2.031 (8) Å found in I. This difference is strongly indicative of the greater steric interaction of the *i*-C₃H₇ group compared to that of the CH₃ group, a relationship well-documented in six-coordinate cobaloximes with these R groups.^{37,38}

For III, the geometry of the py—Co—CH₂R' fragment is compared to other B₁₂ models in Table X. As found previously, the Co—N distances in saloph compounds are longer than those in corresponding cobaloxime complexes but are sensitive to the trans influence of R.²³ The Co—C bond distances are insensitive to the nature of the equatorial ligand but are sensitive to both the bulk and electron donor properties of R. In the saloph complexes, the bond distances increase in the order CH₂CN ~ CH₂CF₃ < CH₂CH₃. The Co—C—R' angle appears to more closely follow bulk and increases in the order CH₂CN < CH₂CH₃ < CH₂CF₃. Cobaloximes have similar trends.²² Deviations from planarity of the equatorial moiety are greater for the Schiff base complexes than for the corresponding cobaloximes. This and the above trends have been discussed previously,²³ and the data for compound III are entirely consistent.

Finally, the C—CF₃ group in cobaloximes deviates significantly in terms of both bond angles and lengths from that expected from fluorohydrocarbons. Theoretical calculations demonstrate that this effect can be attributed to the carbanion character of the —CH₂CF₃ ligand.³⁵ The values of the CCF and FCF angles are consistent with moderate carbanion character.³⁵ In this regard, saloph and cobaloximes do not appear to be significantly different.

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(38) Marzilli, L. G.; Toscano, P. J.; Randaccio, L.; Bresciani-Pahor, N.; Calligaris, M. *J. Am. Chem. Soc.* **1979**, *101*, 6754.

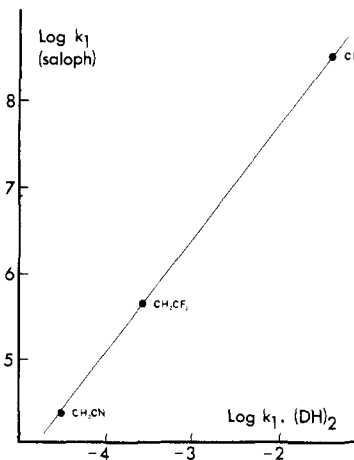


Figure 8. Plot of $\log k_1$ for 3,5-lutCo(saloph)R vs. $\log k_1$ for 4-CNpyCo(DH)₂R.²²

This finding is in keeping with our previous conclusion²³ that the structural features of the Co—R moiety are insensitive to the electronic effect of the equatorial ligand.

Description of the Ligand-Exchange Data. As discussed previously, ligand-exchange rates for saloph compounds exceed those for cobaloximes by many orders of magnitude.²³ This result is an example of the cis effect since only the cis (equatorial) ligand is changed. To the previously reported data for the 3,5-lutCo(saloph)CH₂CN compound, we can now add results for R = CH₂CF₃ and CH₃ (Table VIII). A log-log plot of ligand-exchange rate constants for 4-CNpy cobaloximes and 3,5-lut(saloph) compounds with corresponding R groups is presented in Figure 8. A linear relationship is found with a slope = 1.3. A slope greater than unity means that the relative trans effect of alkyl ligands increases with increasing R electron donation (increasing trans influence and increasing trans effect).

For R = CH₂CF₃ and CH₃ only, a comparison of exactly the same leaving ligand, 3,5-lut, can be made. The ratio of Co(saloph) to Co(DH)₂ rates are 3.2×10^{10} and 8.2×10^{10} , respectively. Although the rate for 3,5-lutCo(DH)₂CH₂CN is too slow to measure reliably, the limited direct comparison supports the synergy between cis and trans effects.

Discussion

The results described above contain information relevant to (a) the relationship between dynamics and structure of Schiff base complexes, (b) the possible existence of stable five-coordinate species for less-electron-rich B₁₂ model and cobalamins, and (c) the role of the 5,6-dimethylbenzimidazole ligand in Co—C bond homolysis in B₁₂ holoenzymes. In this section, these topics will be considered separately.

Dynamics vs. Structure. In the exchange reaction of the neutral axial ligand of organocobalt B₁₂ model compounds, the formation of five-coordinate intermediates is well-documented.¹⁻¹¹ It is logical to assume that in such species of reduced coordination number, steric strain in the six-coordinate species will be relieved.³ The present results provide direct evidence for this phenomenon. In I and II, the Co atom is displaced out of the N₂O₂ equatorial plane and the Co—C bonds are relatively shorter than in relevant six-coordinate complexes with R = CH₃ or *i*-C₃H₇, Table X. Nevertheless, all the steric strain is not relieved since the Co—C bond length in the *i*-C₃H₇ compound I is longer than in II. There is presently no clear published evidence for steric acceleration of ligand-exchange rates by bulky R groups in B₁₂ model compounds.^{8,39} The absence of any appreciable effects can be attributed to several possible causes. First, steric interactions should persist in the activated complex which is likely to be intermediate in geometry to the isolated five- and six-coordinate species although the Co—L bond should be nearly broken in the transition state.^{5,6,8}

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Second, most bulky alkyl groups employed thus far are also good trans influence ligands.⁵⁻⁸ The bond between L and Co is thus longer, and the "effective bulk" of L is decreased.²³ Consequently, any steric effect by R would appear to be reduced. Third, steric interactions in compounds with bulky R lengthens the Co-C bond,²² and the electron donation by R is reduced with a consequent decrease in trans effect.

All the factors which stabilize five-coordinate cobalt(III) complexes are not clear.²³ In our previous analysis of ligand-exchange data for saloph complexes,²³ the relative reactivity of cobaloximes to cobalamins to saloph complexes was estimated to be 1 to 10^7 to 10^{10} . This approximate analysis was for complexes with the relatively poor trans effect ligand CH_2CN , and since we have now shown that the trans effect is a function of the cis effect, the relative reactivity of the saloph to the cobaloxime system with $\text{R} = \text{CH}_3$ is even higher, $\sim 10^{11}$. This relationship between the cis and trans effects was noted earlier for the cis and trans influence, and thus there is parallel behavior in both the solid and in solution.

Based on arguments concerning Co-N bond distances in the solid,²³ we suggested that the high reactivity of the saloph system most probably is both a ground-state effect (the consequence of the cis influence) and a transition-state effect (greater stability of the pseudo-five-coordinate, $\text{L}-\text{Co}(\text{saloph})\text{R}^\ddagger$, activated complex compared to $\text{L}-\text{Co}(\text{DH})_2\text{R}^\ddagger$). Our demonstration of five-coordinate saloph species in the solid clearly supports this suggestion.

The only other ligand exchange results on a comparable Schiff base B_{12} model are the very limited data for $\text{LCo}(\text{acacen})\text{CH}_3$.² We can estimate that the acacen system is roughly 10^2 times more reactive than the saloph system.⁴⁰ The relatively higher reactivity and the stability of five-coordinate complexes are both understandable and well-documented for the acacen system, which is the most "electron rich" of the widely studied model systems.^{2,13-16}

Stable Five-Coordinate Species in Other Model Systems and in Cobalamins. Cobaloximes are possibly the most "electron poor" of the common B_{12} model systems.^{2,13-16} The best evidence for stable five-coordinate cobaloximes has been obtained only in optimal conditions. Thus, $\text{H}_2\text{OC}(\text{DH})_2\text{R}$ complexes appear to dissociate into solvated " $\text{Co}(\text{DH})_2\text{R}$ " in H_2O solution when, as expected, R is a strong trans influence ligand (*i*- C_3H_7 and CH_2CH_3).^{7,8} It was felt that water, a weak ligand, solvated the five-coordinate species. Our results with saloph complexes show that "solvation" by H_2O does stabilize five-coordinate species in the solid state. In nonaqueous solvents, five-coordinate cobaloximes are highly reactive toward formation of the six-coordinate complexes.^{5,6,3} In our view, the evidence for the five-coordinate species of the type " $\text{Co}(\text{DH})_2\text{R}$ " is too indirect, and cobaloximes are too different from cobalamins to be useful in assessing coordination number.

A better model system for comparison to cobalamins is the saloph system investigated here. As for cobaloximes, the best evidence for five-coordinate cobalamins is found when R is a good electron donor (such as *i*- C_3H_7). With a weaker R donor such as CH_3 , the stability of a five-coordinate species is lower. Nevertheless, with the saloph system, such a five-coordinate species exists in the solid. Recent NMR studies on alkyl cobalamins and an X-ray structural study of methylcobalamin (methyl- B_{12}) confirm that except for minor deviations, the relative trans influence of alkyl groups remains the same as in organocobalt B_{12} models.⁴¹ Therefore, the present results are consistent with suggestions that five-coordinate cobalamins exist in aqueous so-

lutions of "base-off" alkylcobalamins where R is a good electron donor.^{12,27,29} Similarly, comparison of NMR and X-ray data for methyl- B_{12} and 5'-deoxyadenosylcobalamin (coenzyme B_{12}) demonstrate that the 5'-deoxyadenosyl ligand has a strong trans influence.⁴¹ Thus, five-coordinate forms of coenzyme B_{12} appear energetically feasible. However, cobalamins and cobinamides are complex molecules with many H bonding side chains.

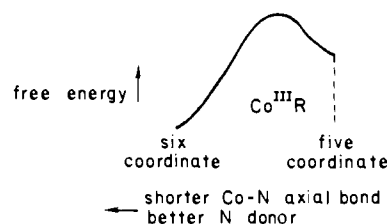
In summary, the results presented here are consistent with the existence of appreciable percentages of five-coordinate forms of cobaloximes, cobinamides, and base-off cobalamins in aqueous solution where one axial ligand is a good electron donor. However, more studies are needed to more fully define the nature of these species in solution and to relate spectral characteristics to structure.

Coordination Number and Co-C Bond Homolysis in B_{12} Holoenzymes. Cobalamins containing sterically bulky R groups are thermally unstable and are readily stabilized in the base-off forms where the pendant 5,6-dimethylbenzimidazole ligand is removed. Spectroscopic studies have provided evidence for a change in coordination number. The understanding of the spectra of these species is still at a primitive stage. The 440-nm band²⁹ mentioned above may not necessarily be indicative of five coordination, and some other feature of the conformationally distorted coenzyme B_{12} in B_{12} holoenzymes⁴²⁻⁴⁶ may be the cause of this band. In addition, the species exhibiting this band may not be kinetically competent.

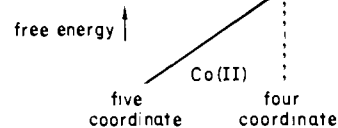
Halpern's work on models demonstrates that poor electron donor ligands trans to R weaken the Co-C bond by destabilizing the Co(III) oxidation state.¹⁶⁻²⁰ However, removal of the trans ligand altogether stabilizes the Co-C bond. We demonstrate here that when R is bulky, the Co-C bond does get shorter in a five-coordinate species. These steric effects may be important. On the other hand, comparison of structural and NMR results for methyl- B_{12} with coenzyme B_{12} (i.e., methylcobalamin vs. 5'-deoxyadenosylcobalamin) does not suggest that the deoxyadenosyl moiety is particularly bulky.⁴¹

Nevertheless, estimates of Co-C bond energies in coenzyme B_{12} ⁴⁷⁻⁴⁹ demonstrate that B_{12} enzymes are able to enhance Co-C bond cleavage rates by a factor of $\sim 10^{10}$. The recent structural studies and Co-C bond energy estimates lead to a qualitative understanding of the importance of structural changes during the cleavage process.

For the ground state, the strength of axial ligation trans to R should have the effect shown below:



For the activated complex, which we approximate as a cobalt(II) species, the following dependence is likely:



A four-coordinate cobalt(II) is probably relatively unstable. Thus,

(40) Reference 2 contains data for (3-Fpy)Co(acacen)CH₃ and (1-(2-(trifluoromethyl)phenyl)imidazolyl)Co(acacen)CH, as well as for the related cobaloximes. Since the data for (3-Fpy)Co(acacen)CH₃ are only approximate, we estimate from the cobaloxime data that the exchange rate for 3-Fpy is ~ 30 times that for an imidazole ligand. A similar ratio is found for comparisons of py to 1-methylimidazole.²² Thus, we estimate that the ligand-exchange rate constant for 3,5-lutCo(acacen)CH₃ is $\sim 10^3 \text{ s}^{-1}$ at -86°C . The measured constant for the relevant saloph compound is 5 s^{-1} at -80°C . Therefore, the factor of 10^2 seems like a conservative estimate.

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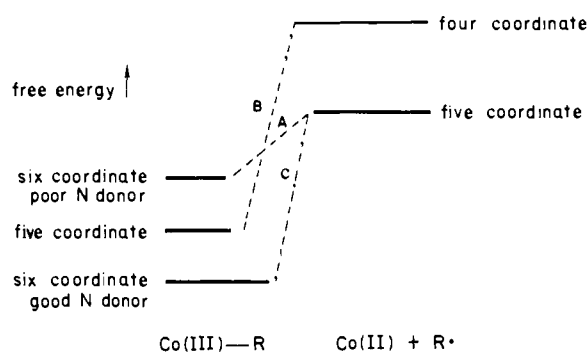
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the Co-C cleavage process would be most facile in a situation where the Co-N bond changes from being a relatively long bond (weak donor) in the still six-coordinate ground state to a relatively stronger bond leading to a five-coordinate Co(II) species, as illustrated schematically below:



The minimum barrier would involve path A, where the 5,6-dimethylbenzimidazole supports formation of the five-coordinate Co(II) species (B_{127}) without stabilizing the six-coordinate Co(III) relative to the five-coordinate Co(III) species. In a six-coordinate species with a weakly bound 5,6-dimethylbenzimidazole, the Co is maintained in the plane defined by the four corrin N atoms, thereby maintaining steric repulsions between the 5'-deoxyadenosyl and the corrin. These steric interactions could be made more severe in the holoenzyme if the protein distorts the corrin.⁴¹⁻⁵¹

(50) A detailed discussion of the relationship between the structure and Co-C bond energy for cobalamins as well as relevant references can be found in ref 22.

Path B, between a five-coordinate cobalt(III) and a four-coordinate cobalt(II) species, is probably the most unfavorable pathway both because the five-coordinate species is stabilized somewhat by the reduction in steric interaction and also because a four-coordinate cobalt(II) species should be relatively unstable. Path C corresponds to free-energy changes expected in models and in cobalamins in the absence of enzymes.

The above qualitative picture requires further investigation of both the energetics and structural changes in models and cobalamins. However, if it represents a reasonable approximation of the interrelationship between structure, coordination number, and axial bond strengths, then the intermediacy of five-coordinate $Co^{III}R$ species in the enzymic process appears unlikely.

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Registry No. I, 98395-46-1; I-1.5H₂O, 98395-47-2; IIA, 98395-54-1; IIB, 32105-85-4; IIB-0.5H₂O, 98395-48-3; III, 90742-75-9; III-0.5H₂O-0.5C₅H₅N, 98395-49-4; B₁₂, 68-19-9; 3,5-lutCo(saloph)CH₂CF₃, 98395-50-7; 3,5-lutCo(saloph)CH₃, 98395-51-8; 3,5-lutCo(DH)₂CH₃, 98395-52-9; 3,5-lutCo(DH)₂CH₂CF₃, 98395-53-0; 3,5-lutCo(saloph)-CH₂CN, 90742-74-8.

Supplementary Material Available: Tables of hydrogen atom coordinates, anisotropic thermal parameters, and structure factors (41 pages). Ordering information is given on any current masthead page.

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Control of the Photochemical Reactivity of Coordination Compounds by Formation of Supramolecular Structures: The Case of the Hexacyanocobaltate(III) Anion Associated with Polyammonium Macrocyclic Receptors

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Abstract: The photochemical behavior of free $Co(CN)_6^{3-}$ and of the adducts obtained from the association of $Co(CN)_6^{3-}$ with diethylammonium ion ($Et_2NH_2^+$), a linear polyammonium ion ($L-21-N_6H_6^{6+}$), and three polyammonium macrocycles ($24-N_6H_6^{6+}$, $32-C_9-N_6H_6^{6+}$, and $32-N_8H_8^{8+}$, Figure 1) has been studied in aqueous solution at room temperature. In all cases a simple photoaquation reaction takes place, with substitution of one CN^- ligand by H_2O . The quantum yield of the photoaquation reaction ($\Phi = 0.30$ for the free $Co(CN)_6^{3-}$ complex) is not affected by the presence of $Et_2NH_2^+$ but decreases when $Co(CN)_6^{3-}$ is associated with polyammonium ions. Specifically, the photoaquation quantum yield drops to 0.15, 0.11, and 0.10 when $Co(CN)_6^{3-}$ is associated with $24-N_6H_6^{6+}$, $32-C_9-N_6H_6^{6+}$, and $32-N_8H_8^{8+}$, respectively. The reduction of the quantum yield is interpreted by assuming that only a discrete number of CN^- are allowed to dissociate in the adducts. This agrees with the formation of adducts of defined molecular structure, in which some of the CN^- ligands are bound to the polyammonium receptor and are thus prevented from escaping when the Co-CN bonds are temporarily broken as a consequence of light excitation. These adducts may be considered as complexes of complexes (or supercomplexes) since the ligands coordinated in the first coordination sphere of the metal in their turn coordinate a macrocyclic ligand. The results obtained indicate that it is possible to protect coordination compounds against ligand photodissociation by using appropriate receptors and they are also promising for other applications related to the control of photochemical reactions.

The photochemical behavior of Werner-type transition-metal complexes has been extensively investigated in the last 25 years,

and the results obtained have given important information on the reactivity of the various types of electronically excited states.²⁻⁴