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Synthesis and Crystal Structure of Organocobalt(III) Complexes with Secondary Alkyls or Bulky Schiff Base Equatorial Ligands

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Alkylcobalt(III) Schiff base B_{12} model complexes with secondary alkyls or a bulky diamine in the equatorial position were synthesized and characterized. Structures have been first determined by X-ray diffraction analysis for i-$C_4H_9Co(salen)(\gamma$-pic) (**I**), n-C_3H_7Co(salen)(γ-pic) (II) and C_2H_5Co(SB) (**III**), where salen = *N,N′*-ethylenebis(salicylideneamine) dianion; SB = 1,1,2,2-tetramethyl-*N,N′*-ethylenebis(salicylideneamine) dianion, γ-pic = γ-picoline. Crystal data for **I** ($CoC_{26}N_3O_2H_{30}$): space group $P2_1/c$ with $a = 6.661(5)$ Å, $b = 18.612(2)$ Å, $c = 19.533(3)$ Å, $\beta = 98.93(1)°$, $V = 2392.10$ Å^3, $D_{calcd} = 1.320$ g·cm^{-3}, $Z = 4$, and $R = 0.048$ for 4469 measured reflections. Crystal data for **II** ($CoC_{25}N_3O_2H_{28}$): space group $P2_1/c$, $a = 9.609(6)$ Å, $b = 19.169(8)$ Å, $c = 12.995(9)$ Å, $\beta = 106.9(7)°$, $V = 2290.4$ Å^3, $D_{calcd} = 1.332$ g·cm^{-1}, $Z = 4$, and $R = 0.048$ for 4358 measured reflections. Crystal data for **III** ($CoC_{22}N_2O_2H_{27}$): space group $P2_1/c$, $a = 8.318(3)$ Å, $b = 21.579(2)$ Å, $c = 11.572(2)$ Å, $\beta = 93.35(1)°$, $V = 2073.7$ Å^3, $D_{calcd} = 1.314$ g·cm^{-1}, $Z = 4$, and $R = 0.060$ for 3954 measured reflections. The crystal structure data reveal that complexes **I** and **II** display six-coordinate octahedral geometry; their Co−C, Co−N bond lengths, as well as the Co-C-C angles, are very close to those in 5′-deoxyadenosylcobalamin. Complex **III** is one of the very few compounds having five-coordinate square pyramidal geometry and observed instability of the Co−C bond.

Introduction

Many organocobalt(III) complexes with a stable σ Co−C bond have been synthesized and investigated.[1−3] Their unusual physico-chemical and structural properties are of considerable interest in B_{12} chemistry.[4] The alkylcobalt(III) Schiff base complexes are one of important kind of coenzyme B_{12} models. They are "electron-rich" systems closer to cobalamins than "electron-poor" cobaloximes.[5] Unfortunately, limited structural data have been reported, especially for the secondary alkyl complexes. Additionally, structurally stable five-coordinate organocobalt(III) complexes which are related to coenzyme B_{12}-dependent enzyme catalytic process are rarely characterized.[6] Only CH_3Co(acacen),[5] [CH_3Co(saloph)]·$0.5H_2O$,[7] [i-C_3H_7Co(saloph)]·$1.5H_2O$,[7] and three alkyl Co(III) complexes with tetraaza dianionic macrocyclic tropocornand as the equatorial ligand[8] were previously isolated, where acacen = ethylenebis(acetylacetone imine) dianion and saloph = *o*-phenylenebis(salicylideneamine) dianion. No five-coordinate salen or substituted salen complexes were reported.

Recently, we have synthesized and characterized two types of alkylcobalt(III) Schiff base B_{12} models. One type is salen complexes RCo(salen)L (R = CH_3, C_2H_5, *n*- and i-C_4H_9, $C_6H_5C_2H_4$; L = H_2O, py, γ-pic). Within this work, two crystal structures, i-$C_4H_9Co(salen)H_2O$[9] and i-C_4H_9Co(salen)py,[10] are reported by us. The second is substituted salen complexes RCo(SB)L (R = CH_3, C_2H_5, n-C_3H_7, i-C_4H_9; L = py, triphenylphosphine (PPh_3), no ligand) with bulky diamine at the quatorial position. In this paper we describe the general preparation methods and the results of X-ray crystal structure analysis for three complexes, i.e., i-C_4H_9Co(salen)(γ-pic) (**I**), C_3H_7Co(salen)(γ-pic) (**II**) and C_2H_5Co(SB) (**III**). Discussions and comparisons of the structure features with those of related complexes as well as 5′-deoxyadenosylcobalamin (DBC) are presented.

Experimental Section

Materials. All chemicals were AR or CP grade. Solvents were dried over appropriate reagents and distilled prior to use.

Instruments. CHN contents of the compounds were determined with a Perkin-Elmer 240 elemental analysis instrument, and the content of Co was determined using an ICP method. ^{1}H NMR spectra were obtained from a Bruker AM-500 spectrometer. IR spectra were

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Table 1. Crystallographic Data for Compounds i-$C_4H_9Co(salen)(\gamma$-pic) (**I**), n-$C_3H_7Co(salen)(\gamma$-pic) (**II**), and $C_2H_5(SB)$ (**III**)

	I	**II**	**III**
formula	$CoC_{26}N_3O_2H_{30}$	$CoC_{25}N_3O_2H_{28}$	$CoC_{22}N_2O_2H_{27}$
mol wt	475.48	461.45	410.41
a, Å	6.661(5)	9.609(6)	8.318(3)
b, Å	18.612(2)	19.169(8)	21.579(2)
c, Å	19.530(3)	12.995(9)	11.572(2)
β, deg	98.93(2)	106.91(7)	93.35(1)
D_{calcd}, g·cm^{-3}	1.320	1.340	1.310
Z	4	4	4
space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
cryst syst	monoclinic	monoclinic	monoclinic
cryst dimens, mm	0.30 × 0.30 × 0.20	0.4 × 0.3 × 0.2	0.10 × 0.20 × 0.30
V, Å^3	2392.1(8)	2290.4(6)	2073.7(7)
data limits	$+h, +k, -l$	$+h, -k, -l$	$+h, -k, -l$
F(000), e	1000	960	864
tot. no. of reflcns	4469	4358	3954
no. of indep reflcns	4221	3978	3560
no. of obsd reflcns ($I > 3\sigma(I)$)	2767	2321	1652
R_{int}[c]	0.049	0.019	0.028
R[a]	0.049	0.048	0.060
R_w[b]	0.052	0.054	0.066
μ, cm^{-1}	7.401	7.707	8.417

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^{0.5}$, where $w = 1/\sigma^2(F)$. [c] R_{int}: agreement between equivalent reflections.

measured on an IR-440 spectrophotometer with KBr pellets. UV−vis spectra were performed on a Shimadzu UV-240 spectrophotometer, equipped with a thermostated cell connected to a circulating constant-temperature bath (25 ± 0.2 °C). TG and DSC were determined on a Perkin-Elmer 7-Series thermoanalysis system under N_2 flow.

Preparation. To avoid Co−C bond cleavage all manipulations were performed in the dark or under a dim red light.

Method A: (1) $RCo(salen)H_2O$ (R = i-C_4H_9, n-C_3H_7, $C_6H_5C_2H_4$) complexes were prepared in accordance with the method described by Schrauzer.[11] Recrystallization was performed in methanol/H_2O with slowly evaporating solvent to obtain the appropriate crystals.

(2) RCo(salen)L (R = i-C_4H_9, n-C_3H_7; L = γ-pic) complexes were prepared by dissolving 60 mg of $RCo(salen)H_2O$ in 10 mL of picoline. After adding 5 mL of light petroleum ether and then allowing the solvents to evaporate slowly at room temperature, we obtained brown or purple crystals in 10 days.

Method B: RCo(SB)L and RCo(SB)(R = CH_3, C_2H_5, n-C_3H_7, i-C_4H_9; L = py, no ligand) complexes were prepared according to the following procedures.

(1) A 2 g sample of SB (6.17 mmol) and 1.5 g (6.31 mmol) of $CoCl_2 \cdot H_2O$ in methanol (80 mL) were stirred for 30 min, and then pyridine was added dropwise (2 mL in 10 mL CH_3OH); the resulting solution was continually stirred for 4 h and then filtered. The solvent was removed by using a rotatory evaporator at room temperature; the residue was washed repeatedly with diethyl ether and dried under vacuum over P_2O_5. The elemental analysis and conductivity measurement prove that the product has the formula $[Co(SB)(py)_2]Cl$.

(2) A 1 g sample of $[Co(SB)(py)_2]Cl$ was dissolved in 60 mL of methanol. Under purging nitrogen, 0.5 g NaOH (in 3 mL of H_2O) and 0.3 g $NaBH_4$ (in 2 mL of H_2O) were added, then 1 mL of 2% $PdCl_2$/ethanol and 1 mL of alkyl halide were injected. After this was stirred for 2 h, 20 mL of acetone was added to destroy excess $NaBH_4$. The solution was filtered and the filtrate reduced in volume. The product was precipitated by adding distilled water. Yield 50−75%. Recrystallization was performed in CH_3OH/H_2O, but in most cases pyridine was lost; only one six-coordinate complex, $CH_3Co(SB)py$, was obtained.

The $CH_3Co(SB)PPh_3$ complex was prepared by using the above procedure.

Crystallographic Data. Data were collected and refined at room temperature (20 °C) on an Enraf Nonius CAD4 four-circle diffractometer by the $\omega/2\theta$ scan mode. Unit cell parameters were determined on the basis of 25 reflections with $9.8 < \theta < 14.2°$. Intensity measurements employed graphite-monochromated Mo Kα (λ = 0.710 73 Å) radiation and $\omega-2\theta$ scan mode in the range $0 < 2\theta < 50°$. During data collection, the intensities of three standard reflections monitored at every 3600 s of X-ray exposure time show no significant decay except for crystal **III**. For crystal **III**, the intensity decreased linearly by 6.1%, but the intensities of the data set were later corrected for this decay. Estimates of agreements between equivalent reflections for **I**, **II**, and III are 2.9%, 2.3% and 2.8%, respectively. Corrections for the presence of extinction for **I** are 3.04×10^{-7} and no corrections for **II** and **III**. After taking into account Lorentz and polarization effects, an empirical absorption correction with minimum 95.67% and maximum 99.89% transmission was applied, based on seven ψ scans. Structure solution by Patterson method revealed the metal atom coordinates, and subsequent difference Fourier methods yielded the positions of all remaining non-H atoms and most of hydrogen atoms. High thermal motion was noted for methyl carbon atoms, C202 and C402 of crystal **III**. A disordered model was applied to C202* and C404*, two alternate positions, each with 50% occupancy, were refined isotropically. Other non-H atoms were refined anisotropically by unit-weighted, full-matrix least-squares techniques. The calculated hydrogen atom positions were allowed to vary with the related carbon atoms; the C−H distance was fixed at 0.95 Å and the isotropic thermal parameters at 4.0 Å. All computations were performed on a Micro VAX-II computer with SDP and ORTEP programs.[12a,b] Atomic scattering factors for neutral atoms were taken from ref 12c. Crystallographic data for **I**−**III** are given in Table 1.

Results and Discussion

Synthesis and Characterization. Alkylcobalt(III) Schiff base complexes are difficult to prepare and purify. Since 1970 only a few six-coordinate alkylcobalt(III) salen and saloph complexes have been structurally characterized.[5] Neither secondary alkylcobalt(III) complexes nor bulky diamine Schiff base B_{12} models have been reported.

In our laboratory, three isobutyl salen derivatives with different axial groups (H_2O, py, γ-pic), one phenylethyl salen complex with H_2O and one propyl salen complex with γ-pic as the axial bases were prepared and their crystal structures were determined. Also, a series of alkylcobalt complexes with bulky 2,3-dimethyl-2,3-butanediimine at the equatorial positions were synthesized. In this paper, the detailed procedures of two general synthetic routes are reported. Method A was used to

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Table 2. Analytical and Physical Measurement Data for RCo(salen)L and RCo(SB)L

formula	anal.,[a] % C	H	N	Co	UV−vis λ, nm (log ϵ)	
i-C$_4$H$_9$Co(salen)(γ-pic) (**I**)	65.71	6.26	8.91	12.12	334 (4.05)	383 sh (3.80)
	65.68	6.36	8.84	12.39	441 sh (3.37)	526 sh (3.06)
n-C$_3$H$_7$Co(salen)(γ-pic) (**II**)	65.34	6.18	9.26	12.93	334 (3.86)	387 sh (3.64)
	65.07	6.12	9.11	12.77	439 sh (3.32)	519 sh (2.97)
C$_6$H$_5$C$_2$H$_4$Co(salen)H$_2$O	63.77	5.17	6.53	13.50	334 (3.96)	386 sh (3.77)
	64.27	5.62	6.25	13.14	435 sh (3.46)	526 sh (3.06)
C$_2$H$_5$Co(SB) (**III**)	63.12	6.59	6.92	13.92	335 (4.28)	393 sh (3.83)
	64.37	6.63	6.82	14.36	462 sh (3.39)	662 (3.19)
CH$_3$Co(SB)py	63.08	5.99	8.72	11.94	333 (4.21)	384 (3.85)
	65.68	6.36	8.84	12.39	437 sh (3.48)	650 (3.18)
n-C$_3$H$_7$Co(SB)	64.35	6.04	8.58	13.39		
	65.07	6.89	6.60	13.88		
i-C$_4$H$_9$Co(SB)	65.18	7.11	6.37	13.67		
	65.73	7.12	6.39	13.44		
CH$_3$Co(SB)PPh$_3$	72.86	6.64	4.79	8.81		
	71.23	5.98	4.26	8.96		

formula	MW	heating temp range, °C	lost wt, % found	calcd	lost substance	DSC peak temp, °C
i-C$_4$H$_9$Co(salen)(γ-pic) (**I**)	475.48	100−149	18.9	19.59	γ-pic	142
		149−174	10.1	12.01	i-C$_4$H$_9$	167
n-C$_3$H$_7$Co(salen)(γ-pic) (**II**)	461.45	100−149	18.9	20.18	γ-pic	136
		149−199	10.1	9.34	n-C$_3$H$_7$	194
C$_2$H$_5$Co(SB) (**III**)	410.50	120−200	6.9	7.07	C$_2$H$_5$	157

[a] First value for each compound in each column is the found value; the second value is the calculated value.

prepare salen analogues, in which RCo(salen)H$_2$O was first prepared, and then the axial H$_2$O was replaced by picoline in methanol/petroleum ether. Method B for RCo(SB) required the preparation of pyridine precursors, which was similar to the preparation of RCo(DH)$_2$PPh$_2$ (DH = monoanion of dimethylglyoxime).[13] By using method B we succeeded in preparing CH$_3$Co(SB)py, but in the case of R = C$_2$H$_5$, n-C$_3$H$_7$, and i-C$_4$H$_9$, axial pyridine was lost during recrystallization to give rise to corresponding base-free five-coordinated complexes RCo(SB) as alkylcobalt(III) saloph complexes.[14] Among these only brown C$_2$H$_5$Co(SB) was suitable for X-ray structure analysis. Attempts to prepare RCo(SB)pph$_3$ were successful only for R = CH$_3$. Unfortunately, no high-quality crystals of CH$_3$Co(SB)PPh$_3$ suitable for X-ray determination were obtained. All RCo(salen)L and RCo(SB)L complexes were characterized by elemental analysis, ^{1}H NMR, UV-vis, IR, and TG-DSC. Part of analytical data and physical measurements are listed in Table 2. It can be seen from the DSC data that C$_2$H$_5$Co(SB) has the lowest temperature for Co−C bond cleavage. The observed instability of the Co−C bond in **III** may be related to the steric interaction between equatorial and axial ligands, i.e., the bulky diamine with the alkyls.

Structure of Complexes. The positional parameters and equivalent isotropic temperature parameters of non-hydrogen atoms are collected in Table 3. Structures of the complexes are shown in Figures 1−3, which includes the atom labelling scheme.

In the six-coordinate i-C$_4$H$_9$Co(salen)(γ-pic) (**I**) and n-C$_3$H$_7$Co(salen)(γ-pic) (**II**), cobalt atom exhibits a distorted octahedral stereochemistry, the salen ligand has the N$_2$O$_2$ coordinated in the equatorial plane. The R (i-C$_4$H$_9$ or n-C$_3$H$_7$) and L (γ-pic) groups occupy the two opposite axial positions. The orientation of the pyridine plane is almost perpendicular to the equatorial salen and parallel to the direction of N$_1$−N$_2$, which is the same as CH$_2$CNCo(saloph)py and different from C$_2$H$_5$Co(saloph)py; in the latter the py plane is only slightly rotated with respect to the N$_2$-O$_1$ direction.[14] In contrast, the five-coordinate C$_2$H$_5$Co(SB) complex assumes a distorted square pyramidal stereochemistry with the SB ligand at the basal plane and the C$_2$H$_5$ group at the apex. Although only a few five-coordinate organocobalt complexes have been reported, their common feasures are a square-pyramidal geometry with a short Co−C bond distance and Co atom displacement out of the coordination plane toward the alkyl group.

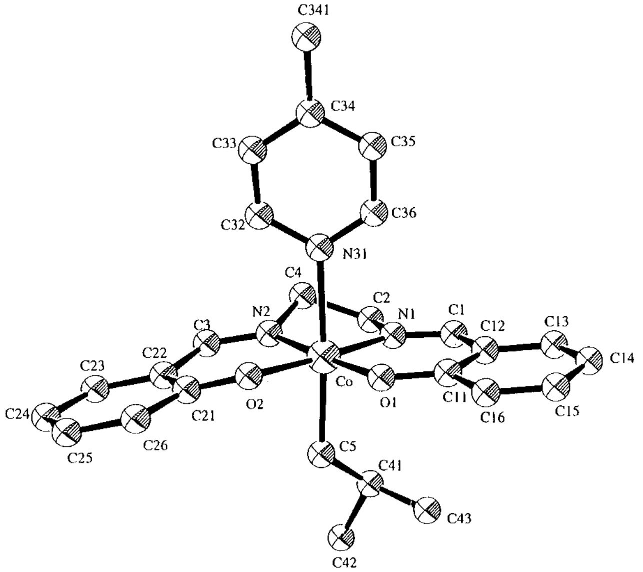

Figure 1. Crystal structure of i-C$_4$H$_9$Co(salen)(γ-pic)(CoC$_{26}$N$_3$O$_2$H$_{30}$) (**I**).

Selected bond distances and bond angles are given in Tables 4−6. Complete data are given in the Supporting Information. Comparisons of bond distances and bond angles around the cobalt between **I**, **II**, **III**, and other organocobalt complexes are listed in Table 7. It can be seen from Table 7 that the axial $\angle$C$_5$−Co−N for **I** and II are 175.5(2)° and 177.0(2)° respectively, which are similar to those in other six-coordinate cobalt(III) saloph, salen, and DH complexes. The $\angle$Co−C$_5$−C

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Table 3. Positional Parameters and Equvialent Isotropic Temperature Parameters with Their Estimated Standard Deviations of Non-Hydrogen Atoms for Compounds *i*-C_4H_9Co(salen)(γ-pic) (**I**), *n*-C_3H_7Co(salen)(γ-pic) (**II**), and C_2H_5Co(SB) (**III**)[a−c]

atom	*x*	*y*	*z*	*B*(eq), Å^2	atom	*x*	*y*	*z*	*B*(eq), Å^2
i-C_4H_9Co(salen)(γ-pic) (**I**)									
Co	0.20321(9)	0.20346(4)	0.28221(3)	2.67(1)	C(16)	0.4395(8)	0.0326(3)	0.1832(3)	3.7(1)
O(1)	0.3603(5)	0.1300(2)	0.2492(2)	3.31(7)	C(21)	0.4564(7)	0.2724(3)	0.3950(2)	2.9(1)
O(2)	0.4466(4)	0.2319(2)	0.3402(2)	2.96(7)	C(22)	0.2946(7)	0.3160(3)	0.4108(2)	3.0(1)
N(1)	0.0360(6)	0.1784(2)	0.2233(2)	3.31(9)	C(23)	0.3226(8)	0.3603(3)	0.4701(3)	3.9(1)
N(2)	0.0533(5)	0.2787(2)	0.3123(2)	3.21	C(24)	0.505(1)	0.3616(3)	0.5135(3)	4.6(1)
N(31)	0.2840(6)	0.2772(2)	0.2007(2)	3.12(8)	C(25)	0.6642(9)	0.3198(3)	0.4985(3)	4.5(1)
C(1)	−0.0570(7)	0.1293(3)	0.1767(2)	3.6(1)	C(26)	0.6421(8)	0.2758(3)	0.4413(3)	3.7(1)
C(2)	−0.2139(8)	0.2224(3)	0.2345(3)	4.5(1)	C(32)	0.3670(7)	0.3419(3)	0.2176(3)	3.4(1)
C(3)	0.1039(7)	0.3204(3)	0.3653(2)	3.4(1)	C(33)	0.4387(9)	0.3867(3)	0.1710(3)	4.2(1)
C(4)	−0.1386(7)	0.2932(3)	0.2654(3)	4.5(1)	C(34)	0.4291(9)	0.3656(3)	0.1029(3)	4.8(1)
C(5)	0.1497(9)	0.1394(3)	0.3613(3)	4.7(1)	C(35)	0.341(1)	0.3000(4)	0.0849(3)	5.0(1)
C(11)	0.2982(7)	0.0838(3)	0.2004(2)	3.1(1)	C(36)	0.2730(8)	0.2575(3)	0.1345(3)	3.9(1)
C(12)	0.0986(7)	0.0822(3)	0.1622(2)	3.3(1)	C(41)	0.022(1)	0.0871(4)	0.3562(4)	7.3(2)
C(13)	0.0503(9)	0.0319(3)	0.1083(3)	4.4(1)	C(42)	0.084(1)	0.0752(6)	0.4255(5)	17.1(3)
C(1′)	0.190(1)	0.0155(3)	0.0921(3)	4.8(1)	C(43)	0.025(2)	0.0169(5)	0.3307(5)	13.1(4)
C(15)	0.3860(9)	−0.0157(3)	0.1302(3)	4.5(1)	C(341)	0.509(1)	0.4124(4)	0.0496(3)	8.1(2)
n-C_3H_7Co(salen)(γ-pic) (**II**)									
Co	0.07067(8)	0.18743(4)	0.41753(6)	3.08(1)	C(22)	0.3036(6)	0.2994(3)	0.5550(5)	3.9(1)
O(1)	0.0349(4)	0.1481(2)	0.2774(3)	3.58(9)	C(23)	0.4129(8)	0.3444(4)	0.6210(6)	5.4(2)
O(2)	0.2098(4)	0.2451(2)	0.3819(3)	3.69(9)	C(24)	0.5239(8)	0.3685(4)	0.5834(6)	6.2(2)
N(1)	−0.0651(5)	0.1298(3)	0.4552(4)	4.3(1)	C(25)	0.5326(7)	0.3488(4)	0.4861(6)	5.8(2)
N(2)	0.0949(5)	0.2301(3)	0.5508(4)	3.9(1)	C(26)	0.4288(6)	0.3069(4)	0.4188(5)	4.5(1)
N(31)	−0.0935(5)	0.2660(3)	0.3473(4)	3.4(1)	C(32)	−0.2283(6)	0.2492(3)	0.2854(5)	4.1(1)
C(1)	−0.1330(6)	0.0776(3)	0.4007(5)	4.5(1)	C(33)	−0.3322(6)	0.2996(4)	0.2428(5)	4.9(2)
C(2)	−0.0780(9)	0.1435(5)	0.5620(6)	8.0(2)	C(34)	−0.3034(7)	0.3687(4)	0.2646(5)	4.6(2)
C(3)	0.1941(7)	0.2743(4)	0.6001(5)	4.3(1)	C(35)	−0.1623(7)	0.3856(4)	0.3247(5)	4.5(2)
C(4)	−0.0152(7)	0.2095(5)	0.6030(5)	6.9(2)	C(36)	−0.0643(6)	0.3328(3)	0.3634(5)	4.0(1)
C(11)	−0.0447(6)	0.0938(3)	0.2399(5)	3.3(1)	C(5)	0.2298(7)	0.1191(4)	0.4856(6)	5.7(2)
C(12)	−0.1265(6)	0.0565(3)	0.2969(5)	3.6(1)	C(41)	0.295(1)	0.0716(7)	0.430(1)	4.4(3)*
C(13)	−0.2090(7)	−0.0018(3)	0.2467(6)	4.8(2)	C(41)*	0.318(2)	0.0997(8)	0.388(1)	5.9(3)*
C(14)	−0.2137(7)	−0.0230(4)	0.1478(6)	5.6(2)	C(42)	0.416(2)	0.112(1)	0.395(2)	9.4(6)*
C(15)	−0.1370(7)	0.0138(4)	0.0898(6)	5.3(2)	C(42)*	0.470(2)	0.0972(9)	0.434(1)	7.0(4)*
C(16)	−0.0535(7)	0.0708(3)	0.1365(5)	4.2(1)	C(341)	−0.4161(8)	0.4258(4)	0.2267(8)	8.4(3)
C(21)	0.3093(6)	0.2825(3)	0.4516(5)	3.4(1)					
C_2H_5Co(SB) (**III**)									
Co	0.0224(1)	0.16171(4)	0.44726(8)	2.97(2)	C(16)	−0.077(1)	0.0787(5)	0.1290(8)	5.0(2)
O(1)	0.0005(7)	0.1383(3)	0.2918(4)	3.9(1)	C(21)	0.2589(9)	0.2577(4)	0.4566(7)	3.0(2)
O(2)	0.1808(6)	0.2153(3)	0.3964(4)	3.7(1)	C(22)	0.2330(9)	0.2713(4)	0.5742(7)	3.1(2)
N(1)	−0.1618(8)	0.1181(3)	0.4876(6)	3.6(2)	C(23)	0.320(1)	0.3182(4)	0.6313(8)	4.0(2)
N(2)	0.0177(8)	0.1981(3)	0.5951(5)	3.4(1)	C(24)	0.437(1)	0.3516(4)	0.5784(8)	4.6(2)
C(1)	−0.237(1)	0.0779(4)	0.4239(8)	4.1(2)	C(25)	0.462(1)	0.3386(5)	0.4615(7)	4.4(2)
C(2)	−0.2266(1)	0.1405(5)	0.5980(7)	7.4(3)	C(26)	0.377(1)	0.2932(4)	0.4027(7)	3.8(2)
C(3)	0.109(1)	0.2418(3)	0.6336(7)	3.4(2)	C(51)	0.295(1)	0.0801(4)	0.4020(8)	6.3(3)
C(4)	−0.106(1)	0.1698(5)	0.6682(7)	7.4(3)	C(201)	−0.356(1)	0.1027(4)	0.644(9)	9.8(4)*
C(5)	0.178(1)	0.0947(5)	0.4926(9)	5.8(2)	C(202)	−0.334(1)	0.2064(6)	0.7708(8)	6.2(3)*
C(11)	−0.092(1)	0.0949(4)	0.2465(8)	3.9(2)	C(202)*	−0.3750	0.193	0.5292	5.7(3)*
C(12)	−0.2060(1)	0.0623(4)	0.3087(7)	3.8(2)	C(401)	−0.143(1)	0.2081(5)	0.7708(8)	6.2(3)*
C(13)	−0.300(1)	0.0164(5)	0.2500(9)	4.7(2)	C(402)	−0.044	0.100	0.718	8.2(7)*
C(14)	−0.285(1)	0.0017(5)	0.139(1)	5.9(3)	C(402)*	−0.007	0.110	0.745	6.6(5)*
C(15)	−0.173(1)	0.0338(5)	0.0771(9)	5.8(3)					

[a] The form of the anisotropic displacement parameter defined as $\exp[-0.25\,(h^2a^2B(1,1) + k^2b^2B(2,2) + l^2c^2B(3,3) + 2hkabB(1,2) + 2hlacB(1,3) + 2klbcB(2,3)]$ where *a*, *b*, and *c* are reciprocal lattice constants. [b] Starred values denote atoms that were refined isotropically. [c] Starred atoms are disordered.

for all complexes deviate significantly from the tetrahedral values. The larger deviations are found in *i*-C_4H_9Co(salen)-H_2O (126.9(8)°), *n*-C_3H_7Co(salen)(γ-pic) (126.1(6)°), and *i*-C_4H_9-Co(salen)(γ-pic) (123.7(9)°). The steric interaction of the *i*-C_4H_9 or *n*-C_3H_7 group with the equatorial moiety provokes a noticeable increase in the Co−C_5−C angle. This has also been observed for analogous cobaloxime complexes CH_2CF_3Co-$(DH)_2PPh_3$ (125.7(9)°) and 5′-deoxyadenosylcobalamin (124.0-(5)°).[15,16] Also, the ∠C_5−Co−N(O)(eq) are significantly distorted from 90° (see Supporting Information). The sum of four angles around the cobalt(∑Co) for all six- and five-coordinate complexes is around 360° as shown in Table 7.

Inspection of Table 7 shows that, for complexes **I**, **II**, **III**, and those six- or five-coordinate alkylcobalt saloph and cobaloxime B_{12} models, relatively little differences are found in the Co−C bond distances, which are all in the range of 1.9−2.0 Å, whereas the Co−C bond distance for $C_6H_5C_2H_4Co$-(salen)H_2O appears significantly shorter than those reported for six-coordinate saloph complexes (1.99−2.042 Å) and our salen complexes (1.992−2.027 Å). This is probably due to some π component caused by a conjugate effect with benzene ring in the carbon atom which is directly linked to the cobalt(III). A similar example has been found for $CH_2{=}CHCo$(salen)py,[17] in which the Co−C(sp^2) bond length is 1.93(2) Å. It is worthwhile

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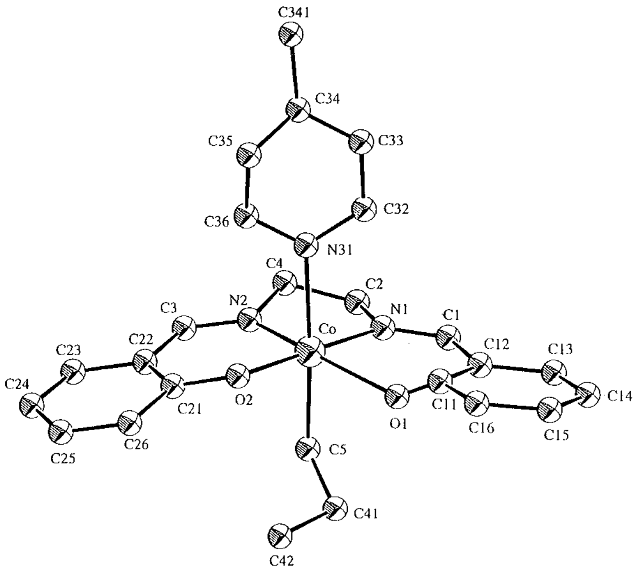

Figure 2. Crystal structure of n-$C_3H_7Co(salen)(\gamma$-pic)($CoC_{25}N_3O_2H_{28}$) (**II**).

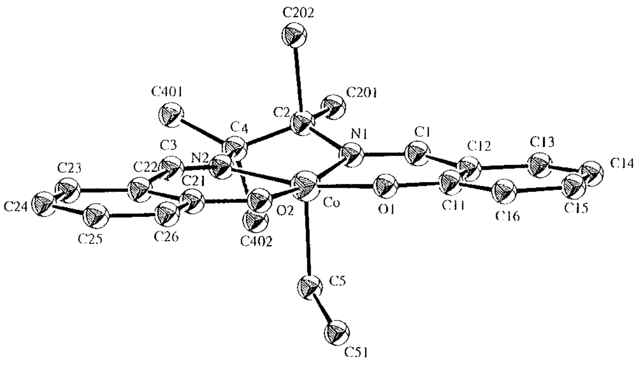

Figure 3. Crystal structure of $C_2H_5Co(SB)$ ($CoC_{22}N_2O_2H_{27}$) (**III**).

to note that results from our CNDO/2 calculations[18] show that the Co−C bond order (or overlap population) for salen and SB complexes have the following order: $C_6H_5C_2H_4Co(salen)(H_2O)$ > i-$C_4H_9Co(salen)(H_2O)$ > $C_3H_7Co(salen)(\gamma$-pic) > i-C_4H_9-Co(salen)py > i-$C_4H_9Co(salen)(\gamma$-pic) > $C_2H_5Co(SB)$. These calculations are consistent with the experimental bond lengths and the DSC data for Co−C bond cleavage listed on Table 2. Comparison of the Co−C bond distance of compound **III** (1.992(7) Å) with those of five-coordinate analogs, CH_3Co-(saloph) (1.960(10) Å) and i-$C_3H_7Co(saloph)$ (2.031(8) Å),[7] suggests that the trend in Co−C lengths is to increase with the order of $CH_3 < C_2H_5 < i\text{-}C_3H_7$, it seems likely that the bulkier and the stronger σ donor properties are the R groups, the longer are the Co−C bond distances in above five-coordinated complexes, although they have different equatorial ligands. Thus, it can be considered that the Co−C bond distance is insensitive to the nature of the equatorial ligand, but sensitive to both the bulk and electron donor properties of R groups as previously observed.[7]

Table 4. Selected Bond Distances (Å) and Bond Angles (deg) for i-$C_4H_9Co(salen)(\gamma$-pic) (**I**)

Co−O(1)	1.896(3)	Co−N(1)	1.873(4)
Co−O(2)	1.903(3)	Co−N(2)	1.867(5)
O1−C(11)	1.302(5)	C(5)−C(41)	1.496(9)
O2−C(21)	1.303(5)	N(1)−C(1)	1.283(6)
N2−C(3)	1.296(7)	N(2)−C(4)	1.477(6)
C34−C(341)	1.51(1)	N(31)−C(32)	1.344(6)
N31−C(36)	1.334(6)	C(41)−C(42)	1.50(1)
C(1)−C(12)	1.419(7)	C(41)−C(43)	1.46(1)
C(2)−C(4)	1.502(8)	C(3)−C(22)	1.435(6)
Co−N(31)	2.230(4)	Co−C(5)	2.027(6)
O(1)−Co−O(2)	86.6(1)	O(1)−Co−N(1)	94.2(2)
O(1)−Co−N(2)	177.5(2)	O(1)−Co−N(31)	89.7(1)
O(1)−Co−C(5)	90.4(2)	O(2)−Co−N(1)	178.0(2)
O(2)−Co−N(2)	93.0(1)	O(2)−Co−N(31)	88.6(1)
O(2)−Co−C(5)	86.8(2)	N(1)−Co−N(2)	86.2(2)
N(1)−Co−N(31)	89.5(2)	N(1)−Co−C(5)	95.1(3)
N(2)−Co−N(31	87.9(2)	N(2)−Co−C(5)	92.1(2)
N(31)−Co−C(5)	175.5(2)	C(1)−N1−C(2)	119.7(4)
C(3)−N(2)−C(4)	118.6(4)	C(32)−N(31)−C(36)	116.2(4)
N(1)−C(1)−C(12)	125.3(4)	N(1)−C(2)−C(4)	108.6(4)
N(2)−C(3)−C(22)	123.7(4)	N(2)−C(3)−C(22)	123.7(4)
N(2)−C(4)−C(2)	107.0(4)	O(1)−C(11)−C(12)	124.2(4)
O(1)−C(11)−C(16)	118.1(5)	C(1)−C(12)−C(13)	118.0(4)
C(1)−C(12)−C(11)	122.4(4)	O(2)−C(21)−C(22)	124.4(4)
O(2)−C(21)−C(26)	118.5(4)	C(3)−C(22)−C(21)	121.9(5)
C(3)−C(22)−C(23)	117.8(4)	N(31)−C(32)−C(33)	123.6(5)
C(35)−C(34)−C(341)	121.0(5)	N(31)−C(36)−C(35)	123.3(5)
C(5)−C(41)−C(42)	110.6(7)	C(5)−C(41)−C(43)	113.7(8)

Table 5. Selected Bond Distances (Å) and Bond Angles (deg) for n-$C_3H_7Co(salen)(\gamma$-pic) (**II**)[a]

Co−O(1)	1.908(3)	Co−O(2)	1.893(3)
Co−N(1)	1.880(4)	Co−N(2)	1.868(4)
Co−N(31)	2.180(4)	Co−C(5)	2.012(5)
O(1)−C(11)	1.301(5)	O(2)−C(21)	1.322(6)
N(1)−C(1)	1.287(6)	N(1)−C(2)	1.453(7)
N(2)−C(3)	1.297(7)	N(2)−C(4)	1.467(7)
C(1)−C(12)	1.428(7)	C(2)−C(4)	1.436(9)
C(5)−C(41′)	1.41(1)	C(5)−C(41)	1.76(1)
C(41)−C(42)	1.57(2)	C(41)*−C(42)*	1.40(2)
O(1)−Co−O(2)	86.7(1)	O(1)−Co−N(1)	94.0(2)
O(1)−Co−N(2)	176.0(2)	O(1)−Co−N(31)	88.0(1)
O(1)−Co−C(5)	93.8(3)	O(2)−Co−N(1)	179.1(2)
O(2)−Co−N(2)	93.7(2)	O(2)−Co−N(31)	88.3(1)
O(2)−Co−C(5)	89.2(3)	N(1)−Co−N(2)	85.8(2)
N(1)−Co−N(31)	92.4(2)	N(1)−Co−C(5)	90.0(2)
N(2)−Co−C(31)	88.0(2)	N(2)−Co−C(5)	90.2(2)
N(31)−Co−C(5)	177.0(2)	C(1)−N(1)−C(2)	119.7(5)
C(3)−N(2)−C(4)	118.2(4)	C(32)−N(31)−C(36)	116.8(4)
N(1)−C(1)−C(12)	125.8(5)	N(1)−C(2)−C(4)	111.9(6)
N(2)−C(3)−C(22)	122.7(5)	N(2)−C(4)−C(2)	110.3(5)
O(1)−C(11)−C(12)	124.2(4)	O(1)−C(11)−C(16)	118.6(4)
C(1)−C(12)−C(13)	119.2(5)	C(1)−C(12)−C(11)	122.2(4)
O(2)−C(2)−C(22)	124.2(5)	O(2)−C(21)−C(26)	117.5(4)
C(3)−C(22)−C(21)	123.7(4)	C(3)−C(22)−C(23)	117.1(5)
N(31)−C(32)−C(33)	121.9(5)	C(35)−C(34)−C(341)	120.0(6)
N(31)−C(36)−C(35)	124.6(5)	C(5)−C(41)−C(42)	108(1)
C(5)−C(41)*−C(42)*	111(1)		

[a] Starred atoms are disordered.

Unlike the Co−C bond, the Co−L bond distance has a strong dependence on the natures of both the equatorial ligand and the R group. Previous data for octahedral salen complexes showed that the Co−N(py) bond distances ranged from 2.031 (R = CH_3O) to 2.184 Å (R = i-C_4H_9),[5,9] for saloph complexes from 2.098 (R = CH_2CN) to 2.215 Å (R = C_2H_5), and for cobaloxime, from 2.028 to 2.099 Å.[5,10,14,19,20] Therefore, the Co−N bonds are much longer in Schiff base complexes than

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Table 6. Selected Bond Distances (Å) and Bond Angles (deg) for $C_2H_5Co(SB)$ (**III**)[a]

Co−O(1)	1.869(4)	Co−O(2)	1.874(4)
Co−N(1)	1.880(5)	Co−N(2)	1.884(5)
Co−C(5)	1.992(7)	O(1)−C(11)	1.305(7)
O(2)−C(21)	1.299(6)	N(1)−C(1)	1.279(7)
N(1)−C(2)	1.492(8)	N(2)−C(3)	1.276(7)
N(2)−C(4)	1.499(7)	C(1)−C(12)	1.414(8)
C(2)−C(4)	1.399(9)	C(2)−C(201)	1.480(8)
C(2)−C(202)	1.754(8)	C(3)−C(22)	1.423(8)
C(2)−C(202)*	1.835(9)	C(4)−C(401)	1.494(9)
C(4)−C(402)	1.678(8)	C(5)−C(51)	1.500(9)
C(4)−C(402)*	1.748		
O(1)−Co−O(2)	84.0(2)	O(1)−Co−N(1)	93.9(2)
O(1)−Co−N(2)	168.9(3)	O(1)−Co−C(5)	94.7(3)
O(2)−Co−N(1)	170.1(2)	O(2)−Co−N(2)	94.6(2)
O(2)−Co−C(5)	94.2(3)	N(1)−Co−N(2)	85.6(2)
N(1)−Co−C(5)	95.7(3)	N(2)−Co−C(5)	96.4(3)
C(1)−N(1)−C(2)	121.8(8)	C(3)−N(2)−C(4)	121.2(5)
N(1)−C(1)−C(12)	126.5(6)	N(1)−C(2)−C(4)	111.5(5)
N(1)−C(2)−C(201)	115.8(5)	N(1)−C(2)−C(202)	100.1(5)
N(1)−C(2)−C(202)*	95.5(6)	C(4)−C(2)−C(201)	123.6(7)
C(4)−C(2)−C(202)	99.4(5)	C(4)−C(2)−C(202)*	114.3(7)
C(201)−C(2)−C(202)*	90.4(6)	C(201)−C(2)−C(202)	101.0(5)
N(2)−C(3)−C(22)	126.7(5)	N(2)−C(4)−C(2)	110.2(5)
N(2)−C(4)−C(401)	113.9(5)	C(2)−C(4)−C(402)*	104.9(5)
C(2)−C(4)−C(402)	89.3(6)	C(401)−C(4)−C(402)*	96.9(5)
C(401)−C(4)−C(402)	107.1(5)	O(1)−C(11)−C(12)	123.5(5)
O(1)−C(11)−C(16)	118.5(6)	C(1)−C(12)−C(11)	121.9(6)
C(1)−C(12)−C(13)	119.6(6)	O(2)−C(21)−C(22)	124.1(6)
O(2)−C(21)−C(26)	118.7(6)	C(3)−C(22)−C(21)	121.6(5)
C(3)−C(22)−C(23)	118.0(5)		

[a] Starred atoms are disordered.

in cobaloximes. At present, the largest Co−N bond distance of known B_{12} models is found in our complex i-$C_4H_9Co(salen)(\gamma$-pic) (2.230(4) Å); the value reported here is the closest to that in coenzyme B_{12} (2.24(1) Å).[16] Likewise, the other bond distances, for example, Co−O(eq), Co−N(eq), C−C, C−O, and C−N, are in good agreement with those reported previously for a wide variety of B_{12} models[2,5] (see Tables 4−6 as well as Supporting Information). Lastly, the unusual bond distances of $C-C_{202}$ and $C-C_{402}$ in **III** are due to the high thermal motion of C_{202} and C_{402} atoms.

Conformational data for six crystals made by us are summarized on Table 8. Information about the extent of coplane of the four coordination atoms, bending angles and torsion angles, the shape of the equatorial ligand and some other parameters was given.

It is interesting to note that the extent of coplane of four coordination atoms $N_1N_2O_1O_2$ is quite good for all six complexes, which was indicated by the values of their mean deviation from the equatorial plane and by the torsion angle NOON as shown in the first two columns of Table 8. However, from d(Co) values of the third column of Table 8, it can seen that in the five-coordinate SB complex the cobalt atom is more displaced from the basal plane toward the apical ligand than it is from the equatorial plane in the six-coordinate salen complexes. Furthermore, the halves of the ethylenebis(salicylideneaminate) moiety are bent toward or away from the axial alkyl group for the salen or substitute salen complexes and assume an umbrella shape ($\gamma = \alpha + \beta$) or a stepped shape ($\beta = \alpha + \gamma$) and a planar shape ($\alpha = \beta = \gamma = 0$).[2] α or β is described by the angle between the $N_1N_2O_1O_2$ coordination plane and the salicylideneamine plane ($O_1C_{11}C_{12}C_{13}C_{14}C_{15}C_{16}C_1N_1$ and $O_2C_{21}C_{22}C_{23}C_{24}C_{25}C_{26}C_3N_2$, respectively). γ is described by the angle between the two salicylideneamine planes. It can be seen from Table 8 that i-$C_4H_9Co(salen)py$ and n-$C_3H_7Co(salen)\gamma$-pic adopt unsymmetrical umbrella-shapes ($\gamma = \alpha + \beta$ and $\alpha \neq \beta$), two i-$C_4H_9Co(salen)L$ (L = H_2O and γ-pic) complexes assume unsymmetrical stepped-shapes ($\beta = \alpha + \gamma$ and $\alpha \neq \gamma$), and $C_6H_5C_2H_5Co(salen)H_2O$ and $C_2H_5Co(SB)$ are

Table 7. Comparisons of Bond Distances (Å) and Bond Angles (deg) around the Cobalt between i-$C_4H_9Co(salen)(\gamma$-pic) (**I**), n-$C_3H_7Co(salen)(\gamma$-pic) (**II**), $C_2H_5(SB)$ (**III**), and Other Organocobalt Complexes

compounds	Co−C	Co−L	∠Co−C_5−C	∠C_5−Co−N_{31}(O)	ΣCo[k]
i-$C_4H_9Co(salen)(\gamma$-pic) (**I**)	2.027(6)	2.230(4)	123.7(9)	175.5(2)	360.4
n-$C_3H_7Co(salen)(\gamma$-pic) (**II**)	2.012(5)	2.180(4)	126.1(6)	177.0(2)	360.2
$C_6H_5C_2H_4Co(salen)H_2O$[a]	1.962(14)	2.209(9)	119.1	176.6(5)	359.6
i-$C_4H_9Co(salen)H_2O$[b]	1.991(9)	2.218(6)	126.9	175.9(4)	359.7
i-$C_4H_9Co(salen)py$[c]	2.003(4)	2.184(3)	115.2	175.3(2)	360.1
$C_2H_5Co(saloph)py$[d]	2.042(6)	2.215(4)	117.3	176.5(2)	
$CH_2CNCo(saloph)py$[e]	2.000(5)	2.098(4)	114.2	177.4(2)	
$CH_2CF_3Co(DH)_2PPh_3$[f]	1.990(10)	2.216(9)	125.7(9)	175.7	363.5
$CH(CN)_2Co(salpn)py$[g]	2.02(1)	2.060(9)		174.9(4)	
DBC[h]	2.00(1)	2.24(1)	124.0(5)	173.0(5)	
$C_2H_5Co(SB)$ (**III**)	1.992(7)		113.9		358.1
$CH_3Co(acacen)$[i]	1.952(18)				
$CH_3Co(saloph)$[j]	1.960(10)				360.0
i-$C_3H_7Co(saloph)$[j]	2.031(8)				358.4

[a] Reference 21. [b] Reference 9. [c] Reference 10. [d] Reference 14. [e] Reference 14. [f] Reference 15. [g] Bailey, N. A.; Higson, B. M.; Mckenzie, E. D. *J. Chem. Soc., Dalton Trans.* **1975**, 1105. [h] Reference 16. [i] Bruckner, S.; Calligaris, M.; Nardin, G.; Randaccio, L. *Inorg. Chim. Acta* **1969**, *3*, 308. [j] Reference 7. [k] ΣCo is the sum of the angles around cobalt.

Table 8. Conformational Data

compound	$N_1N_2O_1O_2$,[a] Å	NOON,[b] deg	d(Co),[c] Å	shape	α,[d] deg	β,[e] deg	γ,[f] deg	φ,[g] deg
i-$C_4H_9Co(salen)H_2O$[9]	0.014	1.1	0.078	stepped	13.2	15.5	2.4	68.7
i-$C_4H_9Co(salen)py$[10]	0.040	3.2	0.029	umbrella	4.1	12.1	16.1	20.4
i-$C_4H_9Co(salen)(\gamma$-pic) (**I**)	0.005	3.8	0.036	stepped	4.6	13.7	9.1	22.1
n-$C_3H_7Co(salen)(\gamma$-pic) (**II**)	0.040	3.2	0.026	umbrella	5.8	12.2	18.0	13.9
$C_6H_5C_2H_4Co(salen)H_2O$[21]	0.010	0.4	0.063	nearly planar	0.9	3.2	3.7	1.7
$C_2H_5Co(SB)$ (**III**)	0.010		0.172	nearly planar	3.6	4.0	1.0	22.3

[a] Mean deviation from the equatorial plane of four donor atoms $N_1N_2O_1O_2$. [b] Torsion angles for $N_1N_2O_1O_2$. [c] Displacements of Co atoms from the $N_1N_2O_1O_2$ plane. [d] Angle between one salicylideneamine residue $O_1C_{11}C_{12}C_{13}C_{14}C_{15}C_{16}C_1N_1$ with the $N_1N_2O_2O_2$ plane. [e] Angle between another salicylideneamine residue $O_2C_{21}C_{22}C_{23}C_{24}C_{25}C_{26}C_3N_2$ with the $N_1N_2O_1O_2$ plane. [f] Angle between the two salicylideneamine residues. [g] Torsion angles for $N_1C_1C_2N_2$.

nearly planar-shaped ($\alpha \approx \beta \approx \gamma \approx 0$). Finally, the bridging ethylene bends away from the ethylenebis(salicylideneaminate) moiety to preserve the approximately gauche conformation, and the ethylene carbon atoms are asymmetrically displaced from the coordination plane (unsymmetrical half-chair conformation).[2] The torsion angles φ around the CH_2-CH_2 bond are listed in Table 8 too. It is worthwhile to note that the best planarity of C_2N_2 was found in $C_6H_5C_2H_4Co(salen)H_2O$, and different deviations were displayed in other complexes.

Conclusion. A series of alkylcobalt(III)−salen or SB coenzyme B_{12} models have been synthesized and characterized. Three crystal and molecular structures have been determined, which are reported here. The interesting features in structure are summarized as follows.

(a) The Co−C bond lengths of three complexes are independent of the nature of the equatorial ligand. However, a slight increase of Co−C bond lengths with the bulk of R group is observed ($C_2H_5 < n\text{-}C_3H_7 < i\text{-}C_4H_9$).

(b) The axial Co−N bond lengths for salen complexes are quite different, which depend on the trans effect of the R groups. It seems likely that the longest Co−N bond distance among Schiff base B_{12} models is found in $i\text{-}C_4H_9Co(salen)(\gamma\text{-pic})$, which is the closest to the corresponding distance in DBC.

(c) The values of $\angle Co-C_5-C$ in all three compounds are larger than ideal tetrahedral value. Such increase seems to be resulted from the steric hindrance of the axial R group. However, the angle in compound **I** is the most similar to that in DBC.

(d) It is worthwhile to note that in the five-coordinate SB complexes weaker Co−C bond may be due to the bulky diamine at equatorial position. Therefore, the structural properties of the complexes are very useful for interpreting the Co−C bond homolysis, the first step in B_{12}-dependent inner-molecular rearrangement reactions.

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Supporting Information Available: Unit cell and pack diagrams of **I**, **II**, and **III** and tables of positional parameters, extensive bond distances and bond angles, least-squares planes, and anisotropic thermal parameters (15 pages). Ordering information is given on any current masthead page.

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