(2) Hexafluoroacetylacetonato(*endo*-η^3-4-methoxy-1,2,3,4-tetraphenylcyclobutenyl)palladium(II). The problems encountered in the purification of the hexafluoroacetylacetonate complexes are due to their very high solubility in organic solvents (even hexanes) which make recrystallization difficult, and their ability to incorporate solvent molecules into the solid state.

Thallous hexafluoroacetylacetonate (0.466 g) and [(*endo*-C$_4$Ph$_4$OMe)PdCl]$_2$ (0.644 g) were stirred in CH$_2$Cl$_2$ (20 mL) for 4 h, then filtered through a short column of Florisil. The evaporation of the filtrate left a yellow, bubbly glass which was pumped overnight under vacuum. The glass was redissolved in hexanes, recolumned (Florisil), evaporated down, and placed under vacuum. [(*endo*-C$_4$Ph$_4$OMe)Pdhfac] was isolated as a yellow glass, mp ~74 °C (0.58 g, 68% yield). Microanalysis (Table I) and the ^{1}H NMR integration supports the incorporation of $^1/_2$ (hexane).

Preparation of the Complexes [(η^1-Dienyl-C$_4$Ph$_4$OR)PdX(Me$_2$PhP)] Where X = acac or hfac (6a–d) or Cl (10). Acetylacetonato(η^1-4-methoxy-1,2,3,4-tetraphenylbutadienyl)dimethylphenylphosphinepalladium(II) (6a). Dimethylphenylphosphine (0.065 mL) in CH$_2$Cl$_2$ (5 mL) was added slowly to a stirred CH$_2$Cl$_2$ solution (10 mL) of [(*endo*-C$_4$Ph$_4$OMe)Pdacac] (0.290 g) under nitrogen. After 10 min the reaction mixture was columned in air through a short column of alumina. The pale yellow eluate isolated by evaporation of the solvent (CH$_2$Cl$_2$) was recrystallized from benzene/cyclohexane to give [(*endo*-C$_4$Ph$_4$OMe)Pdacac(Me$_2$PhP)] as yellow needles (0.240 g, 67% yield). Complexes **6b–d** were prepared in a similar manner from the appropriate acac or hfac complex.

Di-μ-chloro-bis(η^1-4-methoxy-1,2,3,4-tetraphenylbutadienyl)bis-(dimethylphenylphosphine)dipalladium(II) (10). To [(*endo*-C$_4$Ph$_4$OMe)PdCl]$_2$ (0.43 g) in CH$_2$Cl$_2$ (15 mL) under nitrogen was added a solution of Me$_2$PhP (0.112 mL) in CH$_2$Cl$_2$ (5 mL). After 3 min, the solution was opened to the air and evaporated to an orange solid. Recrystallization from benzene/hexane gave [(*endo*-C$_4$Ph$_4$OMe)PdCl(PMe$_2$Ph)]$_2$ as yellow needles (0.45 g, 83% yield).

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Formation of a Cobalt–Carbon Bond under Mild Conditions. Preparation and Crystal Structure of an Acetonyl Adduct of N,N'-Ethylenebis(3-fluorosalicylideniminato)cobalt(II)

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Abstract: The structure of Aquo, acetonyl-N,N'-ethylenebis(3-fluorosalicylideniminato)cobalt(III), crystallized with 0.32 mol of H$_2$O and 0.39 mol of acetone solvate, has been determined from three-dimensional x-ray data collected by counter methods. The compound contains a CH$_3$COCH$_2^-$ group carbon bonded to the cobalt atom; the cobalt–carbon bond was formed under very mild conditions. The material crystallizes in the monoclinic space group $C2/c$ with $a = 18.108$ (4), $b = 13.674$ (2), $c = 18.466$ (3) Å, and $\beta = 118.15$ (2)°. The observed density is 1.52 g/cm^3 and the calculated density is 1.531 g/cm^3 for 8 formula units of CoC$_{16}$H$_{12}$O$_2$N$_2$F$_2$·CH$_2$COCH$_3$·H$_2$O(0.39CH$_3$COCH$_3$)(0.32H$_2$O) in the cell. The structure was refined on F^2 using 2627 unique reflection intensities measured greater than zero; the final conventional R index for all those reflections is 0.051. The geometry of the 3-fluorosalicylideniminato–Co portion of the complex is normal. A water molecule occupies one axial position with the acetonyl group trans to it; the Co–C bond length is 2.01 (1) Å and the Co–O (water) distance is 2.128 (2) Å.

Introduction

The oxygen-carrying cobalt complex N,N'-ethylenebis-(salicylideniminato)cobalt(II) (CoSalen) was synthesized in 1938 by Tsumaki;[1] it has been studied extensively since then.[2,3] Our own efforts have focused on the preparation of crystalline dioxygen adducts of CoSalen and various substituted derivatives. We have succeeded in preparing the monomeric adducts of three substituted complexes and have reported their structures.[4–6] Thus far, the only crystalline complex we have prepared containing the parent compound has been a dimeric species with a dioxygen bridge between the two cobalt atoms.[7]

Table I. Crystal Data for 3-F
CoSalen·CH$_2$COCH$_3$·H$_2$O (0.32H$_2$O)(0.39CH$_3$COCH$_3$)

$a = 18.108$ (4) Å	space group $= C2/c$ (no. 15)
$b = 13.674$ (2) Å	$\rho_{calcd} = 1.531$ g/cm^3
$c = 18.466$ (3) Å	$\rho_{obsd} = 1.52$ g/cm^3
$\beta = 118.15$ (2)°	formula weight = 464.72
$V = 4031$ (2) Å^3	$Z = 8$
$F_{000} = 1896.3$ electrons	

Our attempts to prepare these crystalline monomeric dioxygen complexes have occasionally led to other interesting compounds. In this paper we report the preparation and structure of a novel acetonyl adduct of the 3-fluoro-substituted CoSalen (3-F CoSalen); this adduct bears a resemblance to the coenzymes of naturally occurring vitamin B-12. In contrast to some other organocobalt complexes which are highly reactive, the acetonyl adduct of 3-F CoSalen is stable in air to temperatures as high as 85 °C. The compound forms under mild conditions and shows a lack of chemical reactivity similar to that of the alkylcobaloximes. A preliminary report[8] of a similar complex has been published.

Experimental Section

N,N'-Ethylenebis(3-fluorosalicylideniminato)cobalt(II) was obtained from Dr. E. W. Hughes; the material had been prepared by Professor Calvin's group in the early 1940s[9] and was labeled "#28 3-F slow hydrate". Reagent-grade acetone (50 mL) was placed in a 100-mL volumetric flask and boiled for 10 min to remove oxygen. About 0.05 g of the 3-F CoSalen was added to the boiling acetone and the flask was closed with a serum cap. It was cooled to 3 °C under nitrogen pressure and after 24 h the cap was punctured with a 6-in., 20-gauge hypodermic needle which was left in place. Within 1 week the color of the solution had darkened perceptibly. After 7 weeks at 3 °C, crystals of solvated 3-F CoSalen·CH$_2$COCH$_3$·H$_2$O had formed and were removed. Anal. Calcd for CoF$_2$O$_{4.71}$N$_2$C$_{20.17}$H$_{21.98}$: C, 52.13; H, 4.77; N, 6.03. Found: C, 49.33; H, 4.00; N, 6.42. These analyses (especially for carbon) seem a bit far off, but they were fairly reproducible (e.g., 48.99, 49.67). It is quite possible that there was loss of acetone of crystallization, or incomplete combustion in the microanalyzer even though an oxygen donor (sodium tungstate) was used. Our final formulation is based on the results of the x-ray analysis and not on the elemental analyses.

Crystal Structure Determination. Oscillation and Weissenberg photographs gave preliminary cell dimensions and showed no obvious symmetry. Some preliminary work was done assuming a triclinic cell, but it soon became evident that a monoclinic cell twice the size of the triclinic one was correct. The monoclinic cell dimensions were measured and data were collected on a GE quarter-circle diffractometer automated by Datex. The crystal was a rectangular parallelepiped about $0.07 \times 0.05 \times 0.09$ mm; Co Kα radiation ($\lambda = 1.790\ 21$ Å) was used. Crystal data are given in Table I. Of the 2629 reflections scanned which are space-group allowed, 2627 were observed greater than zero and were used in all calculations. A θ–2θ scan was used at a scan speed of 1°/min, with 30-s background counts taken at each end of the scan. The variances in the intensities, $\sigma^2(I)$ (used to derive the weights for the least-squares refinement), were obtained from counting statistics plus an additional term, (0.02 × scan counts).[2] Because of the small crystal size, no absorption correction was necessary.

Solution and Refinement of the Structure. The coordinates of the cobalt atom were found from a Patterson map and the remaining atoms in the 3-F CoSalen group were located by the usual structure factor–Fourier techniques. The coordinated water molecule was also found, as well as multiple peaks with no obvious interpretation in two contiguous regions of the cell. The atoms which we had located were refined by least squares to convergence with $R_1 = 0.20$ and $R_2 = 0.49$;[10] the confused regions in our Fourier map still had no obvious interpretation. From the map, however, a model was derived containing a disordered acetone O bonded to the Co atom and a solvent acetone disordered about the twofold crystallographic axis. The coordinated acetone appeared to have the O atom and one methyl carbon atom positioned on a line passing through the cobalt atom and roughly perpendicular to the CoSalen plane; the central carbon atom and the other methyl carbon atom showed twofold disorder about this

line. A structure-factor calculation based on this model yielded agreement factors $R_1 = 0.17$ and $R_2 = 0.22$.

The 12 H atoms of the Salen ligand were added as fixed contributions at their calculated positions ($d_{C-H} = 1.00$ Å) and refinement with anisotropic thermal parameters for the remaining atoms of the CoSalen group led to agreement factors $R_1 = 0.08$ and $R_2 = 0.04$. At this point, the isotropic temperature factors of the coordinated acetone suggested that our atom assignments were incorrect. The atom coordinated to cobalt and called oxygen had a temperature factor, B, of 9.3 Å^2, while that of the ordered methyl carbon was 5.8 Å^2, of the disordered central half carbon atoms, 4.7 and 4.0 Å^2, and of the disordered methyl carbons, 3.2 and 2.8 Å^2. These values indicated that the atom bound to cobalt was actually a carbon atom, while the disordered methyl carbon was actually oxygen. A Fourier map of this region reinforced this conclusion; the electron density at the atom bonded to cobalt (actually a carbon) was 5.9 e/Å^3, that at the ordered methyl carbon (a carbon) was 5.3 e/Å^3, at the two central half carbon atoms, 3.2 and 3.3 e/Å^3, and at the disordered methyl half carbon atoms (actually half oxygen atoms), 3.8 and 4.1 e/Å^3. In addition, the torsion angle about the central carbon-"oxygen" bond, which should have been 0 or 180° for an sp^2 oxygen atom, was close to 90° (see the supplementary material, Table 8). The refinement had also shifted the atoms so that the approximate twofold symmetry no longer held, and all four atoms were best represented by pairs of partially occupied sites. Consequently, the atom bonded to cobalt was identified as carbon and the atom with the low temperature factor was identified as oxygen.

Refinement continued using a combination of Fourier, difference-Fourier, and least-squares techniques. Two H atoms of the water molecule trans to the disordered acetonyl group were located in a difference Fourier and added. A persistent peak in the solvent region was identified as a water molecule disordered with respect to the acetone molecule (20% water–80% ½ acetone). Population factors were then allowed to refine, constrained such that (a) the total population of the acetonyl group was unity and (b) the total population of the solvent (½ acetone + one water) was unity. The three terminal atoms of the solvent acetone were assigned a form factor curve representing $\frac{2}{3}$ C + $\frac{1}{3}$ O. The ordered H atoms were allowed to refine isotropically along with anisotropic refinement of the ordered non-H atoms, leading to agreement factors $R_1 = 0.062$ and $R_2 = 0.022$.

Examination of a difference Fourier revealed a peak in the solvent region on the twofold axis which was represented as another water molecule. In addition, the intense low-angle data showed the effects of secondary extinction. These additional parameters were included in the final stages of refinement and, last, the parameters of the disordered atoms separated by less than 1 Å were allowed to refine. Population factors were defined as follows: acetonyl A, X; acetonyl B, $1 - X$; $\frac{3}{2}$ H$_2$O, Y; ½ acetone, $1 - Y$. Parameters were blocked into three matrices as follows: matrix 1, ordered non-H coordinates; matrix 2, ordered non-H thermal parameters, scale factor, and secondary extinction factor; matrix 3, hydrogen coordinates and B's, disordered non-H coordinates and B's, and populations. This final refinement converged with $R_1 = 0.051$ and $R_2 = 0.015$. The goodness of fit is 1.52. The population parameters refined to $X = 0.477$ (6) and $Y = 0.213$ (12) and the secondary extinction factor[11] is 0.87 (8) × 10^{-6}. A final difference Fourier showed nine peaks with $|\rho| \geq 0.3$ e/Å^3; these are listed in the supplementary material.[12] They are all associated with the disordered regions, the three largest being near the solvent acetone. Final parameters are given in Table II; observed and calculated structure factors are available.[12] It is of interest that the disordered atoms refined satisfactorily, even though alternate positions for a given atom were separated by as little as 0.35 (2) Å (C-19A and C-19B). When a refinement has nearly converged, positional and population parameters for atoms such as these can be refined without causing the refinement to diverge.

Description of the Structure. Figure 1 shows the structure of the complex along with the numbering scheme for the coordinated water molecule, the disordered acetonyl group, and the solvent region. The complex shows pseudomirror symmetry with the two halves having almost identical bond lengths and angles (Tables 4 and 5[12]). As a result, these have all been averaged for this discussion. Figure 2 shows the averaged distances and angles pertaining to the axial ligands.

The Acetonyl Group. The striking feature of this compound is the presence of a Co-C bond joining the CoSalen and an acetonyl group. The Co-C distance of 2.01 Å is typical of those found in similar complexes (1.93–2.05 Å),[13] and nearly identical with that in acetonyl

Table II. Final Atomic Parameters[a]

	X		Y		Z		U_{11} or B		U_{22}		U_{33}		U_{12}		U_{13}		U_{23}	
Co	3747.9	(4)	5073.0	(4)	3684.3	(3)	46.5	(4)	40.2	(4)	34.6	(4)	0.1	(3)	12.1	(3)	−2.2	(3)
O1	4181	(2)	6159	(2)	4417	(1)	56	(2)	34	(1)	37	(1)	2	(1)	12	(1)	−2	(1)
O2	3835	(2)	4312	(2)	4595	(1)	56	(2)	36	(1)	38	(1)	−5	(1)	19	(1)	−3	(1)
O3	4997	(2)	4648	(2)	4012	(2)	51	(2)	43	(2)	41	(2)	−1	(1)	13	(1)	−3	(1)
N1	3341	(2)	4022	(2)	2944	(2)	50	(2)	47	(2)	36	(2)	−3	(2)	14	(1)	−4	(1)
N2	3748	(2)	5770	(2)	2806	(2)	54	(2)	42	(2)	36	(2)	0	(2)	14	(2)	2	(1)
C1	3104	(3)	4296	(3)	2090	(2)	72	(3)	57	(3)	37	(2)	−7	(2)	19	(2)	−6	(2)
C2	3666	(3)	5120	(3)	2136	(2)	80	(3)	60	(3)	40	(2)	0	(2)	26	(2)	−1	(2)
C3	3852	(3)	6687	(3)	2765	(2)	58	(3)	58	(3)	44	(2)	−1	(2)	19	(2)	8	(2)
C4	4006	(2)	7387	(3)	3396	(2)	48	(2)	44	(2)	48	(2)	0	(2)	15	(2)	6	(2)
C5	4040	(3)	8387	(3)	3244	(3)	65	(3)	51	(3)	64	(3)	−4	(2)	22	(2)	10	(2)
C6	4208	(3)	9074	(3)	3833	(3)	72	(3)	40	(3)	90	(4)	−5	(2)	27	(3)	7	(3)
C7	4361	(3)	8787	(3)	4615	(3)	71	(3)	42	(2)	76	(3)	−5	(2)	29	(3)	−11	(2)
C8	4338	(3)	7820	(3)	4768	(3)	56	(2)	50	(3)	54	(2)	1	(2)	20	(2)	−4	(2)
C9	4169	(2)	7070	(3)	4197	(2)	42	(2)	40	(2)	53	(2)	3	(2)	14	(2)	0	(2)
C10	3222	(2)	3139	(3)	3097	(2)	52	(2)	48	(2)	44	(2)	−8	(2)	17	(2)	−12	(2)
C11	3376	(2)	2780	(3)	3888	(2)	46	(2)	42	(2)	50	(2)	−6	(2)	18	(2)	−7	(2)
C12	3230	(3)	1788	(3)	3962	(3)	66	(3)	46	(2)	60	(3)	−10	(2)	24	(2)	−8	(2)
C13	3349	(3)	1389	(3)	4680	(3)	80	(3)	45	(2)	76	(3)	−14	(2)	32	(3)	1	(2)
C14	3630	(3)	1981	(3)	5366	(3)	73	(3)	58	(3)	61	(3)	−5	(2)	36	(2)	8	(2)
C15	3785	(2)	2937	(3)	5307	(2)	55	(2)	50	(2)	49	(2)	−2	(2)	26	(2)	−2	(2)
C16	3665	(2)	3398	(3)	4582	(2)	40	(2)	46	(2)	44	(2)	0	(2)	20	(2)	0	(2)
F8	4497	(2)	7536	(2)	5535	(1)	105	(2)	55	(2)	54	(1)	−5	(1)	33	(1)	−12	(1)
F15	4082	(2)	3513	(2)	5992	(1)	93	(2)	60	(2)	48	(1)	−6	(1)	39	(1)	−5	(1)
C17A	2597	(6)	5617	(8)	3318	(6)	3.3	(2)										
C18A	2322	(6)	5315	(8)	3870	(6)	5.1	(2)										
C19A	2515	(9)	5909	(11)	4661	(9)	4.7	(3)										
O4A	1860	(5)	4617	(6)	3743	(5)	6.6	(2)										
C17B	2539	(6)	5319	(8)	3384	(6)	4.1	(2)										
C18B	2460	(5)	6140	(7)	3895	(5)	4.8	(2)										
C19B	2740	(10)	6015	(13)	4811	(10)	7.1	(5)										
O4B	2278	(4)	6961	(5)	3600	(4)	6.6	(2)										
A1	1033	(11)	6960	(13)	2874	(11)	10.8	(5)										
A2	247	(10)	6658	(13)	2486	(13)	7.9	(4)										
A3	−8	(11)	5820	(10)	2243	(9)	8.9	(4)										
A4	−221	(17)	7551	(21)	2371	(17)	12.6	(9)										
W1	644	(14)	6316	(16)	2075	(14)	9.2	(8)										
W2	0		7788	(37)	2500		8.2	(11)										
H1A	319	(2)	373	(2)	185	(2)	3.5	(8)										
H1B	252	(2)	449	(3)	180	(2)	4.8	(9)										
H2A	344	(2)	542	(3)	169	(2)	5.1	(9)										
H2B	420	(3)	486	(3)	232	(3)	6.1	(11)										
H3	386	(2)	689	(2)	234	(2)	4.0	(8)										
H5	396	(2)	852	(3)	275	(2)	4.6	(9)										
H6	423	(3)	975	(4)	371	(3)	9.5	(15)										
H7	441	(2)	925	(3)	502	(2)	5.0	(9)										
H10	301	(2)	267	(3)	260	(2)	4.9	(9)										
H12	308	(3)	140	(3)	352	(2)	5.6	(1)										
H13	332	(3)	75	(3)	476	(3)	6.9	(11)										
H14	369	(3)	175	(3)	582	(2)	5.1	(9)										
HX	511	(3)	421	(4)	432	(2)	7.5	(12)										
HY	529	(3)	519	(3)	419	(3)	7.0	(12)										
H17A1	222		540		278		4.3											
H17A2	261		631		330		4.3											
H17B1	230		474		346		5.1											
H17B2	223		548		282		5.1											

[a] Values in parentheses in all the tables are estimated standard deviations. Anisotropic temperature factors are of the form $\exp[-2\pi^2 (U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hl\,a^*c^* + 2U_{23}klb^*c^*)]$. Coordinates of the nonhydrogen atoms have been multiplied by 10^4, the U_{ij}'s and the hydrogen atom coordinates by 10^3. Hydrogen atom numbers in the Salen group correspond to the carbon atom to which each is attached.

CoSalen methanol.[8] The C=O and C–C distances are within the limits we expect for a ligand comprised of half-populated sites. An infrared spectrum of the complex (Nujol mull) shows two distinct C=O stretches, one at 1659 cm^{-1} (not present in the starting material) for the coordinated acetonyl group and the other at 1716 cm^{-1} for the acetone of crystallization.

The two conformations of the acetonyl group are essentially identical, the only difference being in their interactions with the solvent. The distances and angles are close to those found in acetone; the angle at C17 is reasonable for an sp^3 carbon. The large torsion angle about

(Co–C17–C18–O4) (av 81°) confirms that the atom bonded to cobalt is not sp^2 hybridized.

3-F CoSalen Group. The numbering scheme for the 3-F CoSalen group, along with averaged distances and angles, is shown in Figure 3. Bond lengths and angles are almost identical with those observed in similar structures,[7] but deviations from planarity are much greater. These deviations are best described as a step-shaped conformation for the salicylaldimine residues with respect to the cobalt coordination plane. The conformations are described in terms of the angles α, β, and γ where α and β are the angles which the salicylaldimine residues
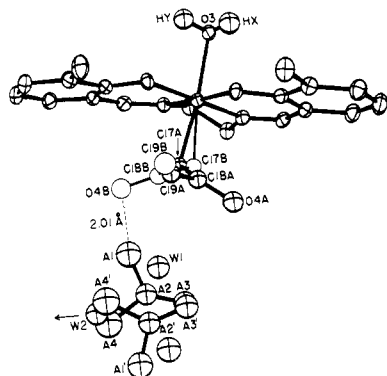
Figure 1. Numbering scheme for the axial ligands and disordered solvent region. Hydrogen atoms (except on OH_2) have been omitted for clarity.
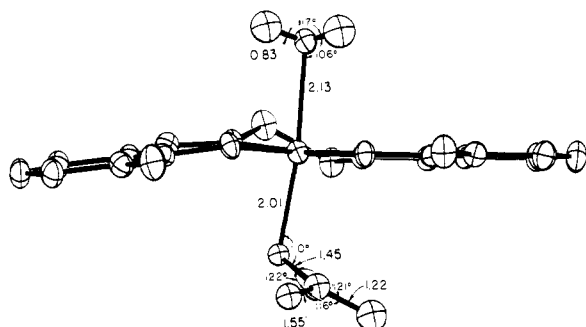

Figure 3. Bond distances and angles (averaged) in the Salen ligand and the hydrogen bonding.

Figure 2. Distances and angles (averaged) pertaining to the axial ligands. The "stepped" arrangement of the Salen ligand can be seen.

Figure 4. Perspective view of the hydrogen-bonded "dimer".

make with the cobalt coordination plane and γ is the angle between the residue planes.[13] For the stepped conformation $\beta \approx \alpha + \gamma$. For acetonyl Co(3-F Salen)OH_2, $\alpha = 4.3°$, $\beta = 12.0°$, and $\gamma = 8.5°$. In addition, there is a slight twist along the long axis of the ligand, probably due to the nonplanar ethylene bridge.

Further evidence of flexibility at the C1-C2 bond and across the cobalt atom is found in the results of a rigid-body analysis.[14] Each of the salicylaldimine residues fits a rigid-body model quite well (root mean square $\Delta U_{ij} = 0.003$), whereas attempts to fit the entire CoSalen molecule resulted in only a fair fit (root mean square $\Delta U_{ij} = 0.004$). In view of the small thermal parameters, no corrections to the calculated bond distances for thermal motion were made.

Coordinated OH_2. H Bonding. The Co-O distance of 2.13 Å is shorter than that observed in the related acetonyl-CoSalen-MeOH complex (2.20 Å)[8] but it is significantly longer than a Co-OH_2 bond in a typical inorganic complex. This bond lengthening is almost surely due to the strong trans influence of the Co-C bond, which has been observed to cause lengthening in many cases.[15] The OH_2 group participates in hydrogen bonding to the Salen O atoms and F atoms of another molecule across a center of symmetry to form a dimer. The distances and angles associated with the interaction are shown in Figure 3 and the overall "dimerization" is shown in Figure 4. Each hydrogen atom forms a bifurcated hydrogen bond with both an F and O atom. The H atom completes trigonal geometry about the Salen oxygen; the C-F · · · H angle is nearly tetrahedral.

Solvent. The solvent region, straddling the twofold axis, consists of one acetone molecule in either of two related positions, or three water molecules, with relative occupancies 79 and 21%, respectively. The oxygen atom in the solvent acetone could not be identified, presumably because of the threefold (or more) disorder at this site. There are no good nearby H-bonding donors to fix the oxygen atom position; we have therefore assumed that the three terminal positions are equally occupied by the oxygen atom and the two carbon atoms. The bond distances we observe reflect this: 1.32, 1.24, and 1.44 Å (C=O in acetone is 1.24 Å and C-C is 1.52 Å). Although it is tempting to assign the atom 1.24 Å from the central carbon as oxygen, we do not believe that the evidence is strong enough to justify this. The acetone interacts with the coordinated acetonyl in that it prevents the "B"
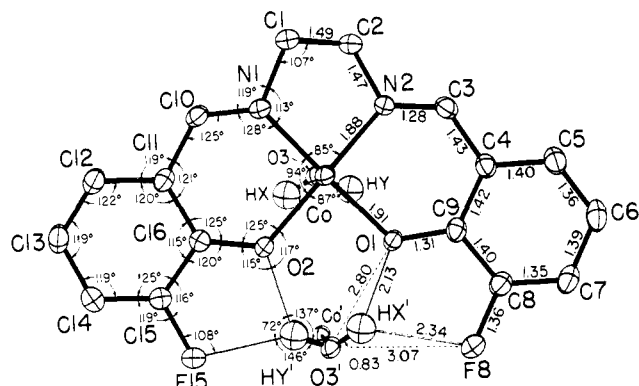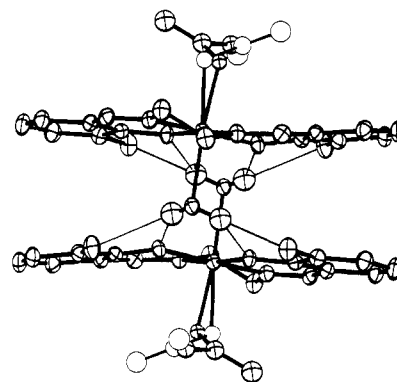
conformation of the acetonyl from existing when the solvent acetone is present in the unprimed position (Figure 1).

Discussion

The feature of greatest interest in this complex is the cobalt-alkyl bond. This formed under mild, quasi-biological conditions, in contrast to the rather vigorous conditions often required to form such bonds (e.g., sodium reduction followed by reaction with an alkyl halide[16]). This facile formation of the acetonyl complex, along with its stability, suggests a certain parallel with vitamin B_{12} chemistry. Such a comparison is useful to some extent. For example, Cob(II)alamin (B_{12r}) has been shown to bind oxygen, just as CoSalen does. One report has suggested that a dimer (Co-O_2-Co) is formed,[17] while another indicated that the adduct was monomeric (CoO$_2$·).[18] Both such adducts have been identified in the CoSalen system as reversible oxygen carriers,[4-7] but neither of these has been observed to react further to form a cobalt-carbon bond.

We believe that the formation of this acetonyl complex involves the transfer of hydrogen from acetone to a coordinated dioxygen intermediate, similar to the mechanism of hydrogen transfer in adenosylcobalamin-dependent rearrangements.[19] This step could be preceded by coordination of the acetone to the cobalt center through the ketone oxygen atom, bringing the C-H bond close to the cobalt atom.[20]
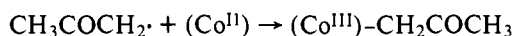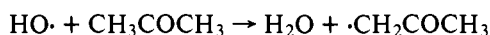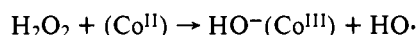

$$\text{(1)}$$
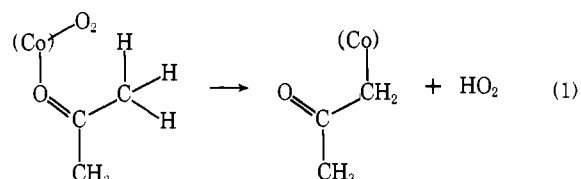
This step could alternatively involve two chelate molecules, one coordinated to the acetone molecule and the other a superoxo-3F CoSalen adduct.

Another possible mechanism involves the enolate form of the acetone.
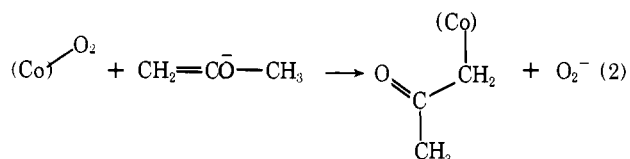
If in either of these cases the reactive cobalt species were dimeric, the leaving dioxygen species would be H_2O_2 or O_2^{2-}. This peroxide could, in turn, lead to formation of the acetonyl adduct by a free-radical pathway.[21]

$$H_2O_2 + (Co^{II}) \rightarrow HO^-(Co^{III}) + HO\cdot$$

$$HO\cdot + CH_3COCH_3 \rightarrow H_2O + \cdot CH_2COCH_3$$

$$CH_3COCH_2\cdot + (Co^{II}) \rightarrow (Co^{III})-CH_2COCH_3$$

In any case, a balanced equation for the formation of the acetonyl complex can be written which does not require the production of any unusual species:

$$2CH_3COCH_3 + 2[Co^{II}] + H_2O + \tfrac{1}{2}O_2$$
$$\rightarrow 2[CH_3COCH_2Co^{III}OH_2]$$
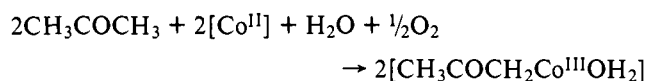
The other CoSalen–acetonyl adduct which has been reported[22] crystallized as a methanol solvate. It was prepared by first forming the Co(III) Salen (aquohydroxo) complex and reacting this with acetone. The acetonyl adduct formed in 0.5 h as a green material which crystallized upon evaporation of solvent. Our synthetic route may amount to essentially the same thing, as our Co(III) intermediate may be formed in situ by air oxidation of the Co(II) Salen starting material. Even so, our product is not green but a deep red-purple. No obvious explanation for the difference in color between these two closely related compounds has presented itself to us. Nonetheless it seems evident that the CoSalen system is suited well to promoting the formation of cobalt–carbon bonds under very mild conditions, in contrast to the vigorous conditions and/or

specialized organic compounds generally needed to produce such compounds. This characteristic seems to be particularly similar to the B_{12} system, which readily activates C–H bonds through cobalt–alkyl bond formation.

Supplementary Material Available: Listing of structure factor amplitudes, and Tables 3 (bond distances), 4 (bond angles), 5 (distances and angles in the hydrogen bonds), 6 (close intermolecular contracts), 7 (residuals in the final difference Fourier), and 8 (torsion angles) (17 pages). Ordering information is given on any current masthead page.

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(10) $R_1 = \Sigma |F_o - F_c| \Sigma F_o$; $R_2 = \Sigma w(F_o^2 - F_c^2)^2 / \Sigma w F_o^4$.
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