

edged. Special thanks are due to Dr. Gregory J. Kubas, Los Alamos National Laboratory, for a gift of $(P(C_6D_{11})_3)_2W(CO)_3(D_2)$ and also for helpful discussions. In addition, we wish to thank Dr. Nita A. Lewis and Daniel Taveras for allowing us

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Registry No. py, 110-86-1; 2,5-Me₂py, 589-93-5; $(P(C_6H_{11})_3)_2W(CO)_3$, 73690-56-9; $P(OMe)_3$, 121-45-9; PPh_2Me , 1486-28-8; $(P(C_6H_{11})_3)_2W(CO)_3(py)$, 100995-31-1; D_2 , 7782-39-0.

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Synthesis and Reactivity of Alkoxide-Bridged Cobaltic Acetates

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Several μ -alkoxy oxo-centered cobalt cluster complexes of formula $[(py)_3Co_3O(OAc)_5OR][PF_6]$, where R = methyl, ethyl, propyl, allyl, benzyl, and 3-phenylpropyl and py = pyridine, were synthesized by treatment of $[(py)_3Co_3O(OAc)_6][PF_6]$ with the alcohol. The 3-phenylpropyl complex [7] was characterized by X-ray crystallographic techniques. At 20 ± 1 °C, the crystal is monoclinic, with $a = 35.684$ (8) Å, $b = 9.691$ (3) Å, $c = 27.134$ (8) Å, $\beta = 102.74$ (2)°, $V = 9152$ (5) Å³, $Z = 8$ [$\mu_a(Mo K\alpha) = 1.19$ mm⁻¹; $d_{calc} = 1.459$ g cm⁻³], and space group $C2/c$ (C_2^2h). The α -hydrogen atoms of the alkoxy ligand display chemical shifts of about 3 ppm upfield from that observed in the uncomplexed alcohol. The complexes decompose thermally to produce mixtures of the aldehyde and the acetate corresponding to the alkoxy ligand.

Introduction

Oxygen-bridged transition-metal cluster complexes are of interest for both theoretical and practical reasons.¹ These complexes offer a fundamental basis to study redox and ligand substitution reactions important to metal-catalyzed autoxidations. We have previously reported² the synthesis and dynamic behavior of several trinuclear oxo-centered and related hydroxy-bridged cobalt cluster complexes. The complexes represent the first trinuclear, oxo-centered cobalt clusters to be completely characterized. These complexes have been found to be interconvertible with one another depending upon the solvent medium.³ Two of these complexes, $[(py)_3Co_3O(OAc)_6][PF_6]$ (1) and $[(py)_3Co_3O(OAc)_5OH][PF_6]$ (2) (py = pyridine), have been isolated from a cobalt-catalyzed autoxidation of alkylaromatics and are, themselves, catalytically active. The catalytic activity and dynamic behavior of these complexes suggest that they are actual catalyst intermediates and are thus excellent model complexes for the oxidation of organic substrates. Herein, we report the synthesis, characterization, and reactivity of a family of oxo-centered cobalt(III) cluster complexes bridged by alkoxy ligands as model compounds to study the oxidation of alcohols.

Experimental Section

Preparation of $[(py)_3Co_3O(OAc)_6][PF_6]$ (1). To a 250-mL flask were added $[(py)_3Co_3O(OAc)_5OH][PF_6]$ (2) (25.0 g, 0.028 mol), acetic acid (90 mL), and acetic anhydride (10 mL). The mixture was boiled for 5 min and allowed to cool to room temperature. The product was collected by filtration, washed with acetic acid (20 mL), and air-dried. The yield was 25.0 g (95%). Anal. Calcd for $C_{27}H_{33}Co_3F_6N_3O_{13}P$: C, 34.88; H, 3.55; N, 4.52. Found: C, 34.46; H, 3.40; N, 4.31. FAB/MS (positive mode) showed the molecular ion at m/e 784.

Preparation of $[(py)_3Co_3O(OAc)_5OCH_3][PF_6]$ (3). **Method I.** To a 125-mL Erlenmeyer flask equipped with a spin bar were added $[(py)_3Co_3O(OAc)_6][PF_6]$ (5.0 g, 5.4 mmol), acetonitrile (40 mL), and methanol (10 mL). The resulting mixture was boiled for 5 min and allowed to cool to room temperature. The solution was layered with diethyl ether (50 mL), and the flask was stoppered and allowed to stand

overnight. The product was collected by filtration and air-dried. The yield was 3.9 g (80%). Anal. Calcd for $C_{26}H_{33}Co_3F_6N_3O_{12}P$: C, 34.63; H, 3.66; N, 4.66. Found: C, 34.33; H, 3.41; N, 4.50. FAB/MS showed the molecular ion at m/e 756. ¹³C NMR (CD_2Cl_2): δ 49.6 (q, OCH_3 , $J_{CH} = 143$ Hz).

Method II. To a 250-mL Erlenmeyer flask equipped with a spin bar was added $Co(OAc)_2 \cdot 4H_2O$ (10.0 g, 40.1 mmol) and 95/5 acetic acid/water (150 mL). Peracetic acid (4.0 mL; 40% solution) was added dropwise to the resulting mixture with stirring. An immediate color change from red to an olive green was observed. The solution was filtered with an additional 1.0 mL of peracetic acid added dropwise to the filtrate. The solution was stripped at room temperature under vacuum to give a green solid (6.91 g), which is crude "cobaltic acetate".

In a 250-mL Erlenmeyer flask equipped with a stir bar, "cobaltic acetate" (2.50 g) prepared from the above method was stirred in methanol (50.0 mL) for 5 min. Pyridine (0.98 g) was added to the reaction, which resulted in a rapid color change from green to brownish green. Addition of NH_4PF_6 (1.00 g), followed by a gentle refluxing for a few minutes, resulted in an immediate precipitation of a brown solid, which was isolated by filtration. Recrystallization of the brown solid in methylene chloride/pentane resulted in 0.34 g of $[(py)_3Co_3O(OAc)_5OCH_3][PF_6]$ with a trace (<1%) of $[(py)_3Co_3O(OAc)_5OH][PF_6]$ as judged by FAB/MS. ¹H and ¹³C NMR spectra were identical with those of the product prepared from $[(py)_3Co_3O(OAc)_6][PF_6]$ and methanol.

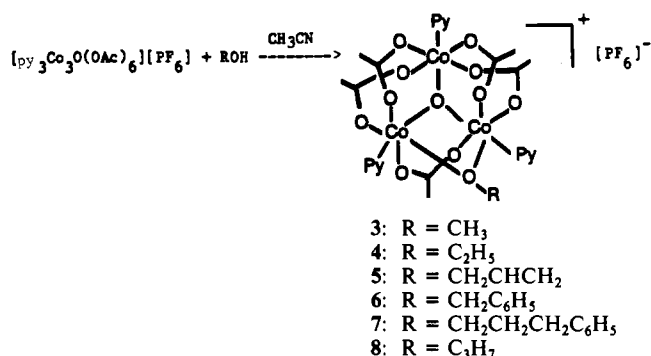
Preparation of $[(py)_3Co_3O(OAc)_5OCH_2CH_3][PF_6]$ (4). To a 100-mL flask equipped with a reflux condenser and spin bar were added $[(py)_3Co_3O(OAc)_6][PF_6]$ (2.0 g, 2.2 mmol), acetonitrile (40 mL), and ethanol (10 mL). The mixture was heated at reflux for 10 min and allowed to cool to room temperature. The product crystallized as long, tan needles, and it was collected by filtration and vacuum-dried. The yield was 1.4 g (61%). Anal. Calcd for $C_{27}H_{35}Co_3F_6N_3O_{12}P$: C, 35.41; H, 3.83; N, 4.59. Found: C, 35.23; H, 3.81; N, 4.39. FAB/MS showed the molecular ion at m/e 770. ¹³C{¹H} NMR (CD_3CN): δ 59.1 and 16.1 (s, 1 C each, OCH_2CH_3).

Preparation of $[(py)_3Co_3O(OAc)_5OCH_2CHCH_3][PF_6]$ (5). To a 100-mL flask equipped with a reflux condenser and spin bar were added $[(py)_3Co_3O(OAc)_6][PF_6]$ (2.1 g, 2.3 mmol), acetonitrile (40 mL), and allyl alcohol (10 mL). The resulting mixture was heated at reflux for 5 min and allowed to cool to room temperature. The solvent was evaporated, and the residue was taken up in methylene chloride, filtered, and layered with petroleum ether. After the mixture was left standing overnight, the product was collected by filtration. The yield was 1.5 g (72%). Anal. Calcd for $C_{28}H_{40}Co_3F_6N_3O_{12}P$: C, 36.05; H, 4.29; N, 4.51. Found: C, 35.29; H, 3.64; N, 4.47. FAB/MS showed the molecular ion at m/e 782. ¹³C{¹H} NMR (CD_3CN): δ 136.2, 116.2, and 65.2 (s, 1 C each, OCH_2CHCH_3).

Preparation of $[(py)_3Co_3O(OAc)_5OCH_2C_6H_5][PF_6]$ (6). To a 100-mL flask equipped with a reflux condenser and spin bar were added

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Scheme I



$[(py)_3Co_3O(OAc)_6][PF_6]$ (2.0 g, 2.2 mmol), acetonitrile (40 mL), and benzyl alcohol (10 mL). The resulting mixture was heated at reflux for 7 min and allowed to cool to room temperature. The acetonitrile was evaporated, and the residue was dissolved in 25 mL of methylene chloride, filtered, and layered with 75 mL of petroleum ether. After the mixture was allowed to stand for 24 h, the product was collected by filtration and vacuum-dried. The yield was 1.3 g (60%). Anal. Calcd for C₃₂H₃₇Co₃F₆N₃O₁₂P: C, 39.30; H, 3.79; N, 4.30. Found: C, 39.00; H, 3.86; N, 4.16. FAB/MS showed the molecular ion at *m/e* 832.

Preparation of $[(py)_3Co_3O(OAc)_3OCH_2CH_2CH_2C_6H_5][PF_6]$ (7). The procedure described above for the preparation of **6** was followed except that 3-phenyl-1-propanol was used in place of benzyl alcohol and the reaction mixture was refluxed for 10 min. The yield was 1.8 g (78%). Anal. Calcd for C₃₄H₄₁Co₃F₆N₃O₁₂P: C, 40.60; H, 4.08; N, 4.18. Found: C, 41.50; H, 4.13; N, 4.02. FAB/MS showed the molecular ion at *m/e* 860. ¹³C{¹H} NMR (CD₃CN): δ 66.1, 25.8, and 25.3 (s, 1 C each, OCH₂CH₂CH₂C₆H₅).

Preparation of $[(py)_3Co_3O(OAc)_3OCH_2CH_2CH_3][PF_6]$ (8). The procedure described above for the preparation of **6** was followed except that 1-propanol was used in place of benzyl alcohol and the reaction mixture was refluxed for 10 min. The yield was 1.7 g (85%). Anal. Calcd for C₂₈H₃₇Co₃F₆N₃O₁₂P: C, 36.17; H, 3.98; N, 4.52. Found: C, 36.16; H, 4.41; N, 4.40. FAB/MS showed the molecular ion at *m/e* 784. ¹³C{¹H} NMR (CD₃CN): δ 66.6, 24.0, and 10.4 (s, 1 C each, OCH₂CH₂CH₃).

Thermal Decomposition of $[(py)_3Co_3O(OAc)_3OR][PF_6]$. To a thick-walled glass ampule were added 0.5 mmol of the alkoxide complex, 0.3 mmol of dimethyl terephthalate (internal standard), and 5 mL of chlorobenzene. The ampule was evacuated and filled with argon three times and finally sealed under vacuum. The resulting sealed ampule was connected to a mechanical shaker arm and immersed in a constant temperature oil bath set at 150 °C. The reaction mixture was shaken while in the bath for 17 h. The resulting mixture was removed from the bath, allowed to cool, and analyzed by gas chromatography using a Hewlett-Packard 5890A gas chromatograph equipped with an automatic injector and a Durabond DB-17 capillary column. For R = C₂H₅, acetaldehyde was detected in about 10% yield and ethyl acetate was found in 88% yield. For R = C₃H₇, the yield of propionaldehyde was 42% and propyl acetate was 13%. Benzaldehyde, benzyl acetate, and benzoic acid were found in 86%, 5%, and 5% yields respectively for R = benzyl. For R = 3-phenylpropyl, the yield of 3-phenylpropionaldehyde was 48%, the yield of 3-phenylpropyl acetate was 5%, and benzaldehyde was observed in 10% yield.

Reaction of Benzyl Alcohol with 1. The procedure described above for the thermal decompositions was followed except that benzyl alcohol (59 mg, 0.55 mmol), and **1** (480 mg, 0.52 mmol) were used in place of the alkoxide complex. The yield of benzaldehyde was 0.42 mmol (75%), and the yield of benzyl acetate was 0.02 mmol (4%).

Reaction of Benzyl Alcohol with 2. The procedure described above for the thermal decompositions was followed except that benzyl alcohol (59 mg, 0.55 mmol), and **2** (467 mg, 0.53 mmol) were used in place of the alkoxide complex. The yield of benzaldehyde was 0.45 mmol (82%), and the yield of benzyl acetate was 0.02 mmol (4%).

Reaction of $[(py)_3Co_3O(OAc)_3(OH)_2][PF_6]$ (9) with Ethanol in Acetic Acid. To a thick-walled glass ampule were added **9** (150 mg, 0.14 mmol), ethanol (1 mL), and acetic acid (1 mL). The ampule was evacuated, sealed, and shaken for 10 min in an oil bath heated to 120 °C. The ampule was removed from the bath and allowed to stand at ambient temperature for 10 days. The contents of the ampule were removed and filtered. The residue was washed with 3 mL c^o water and air-dried (104 mg). The ¹H NMR and FAB mass spectrum showed the residue to be a mixture of **1**, **2**, and **4** in a ratio of 1:1:6, respectively.

X-ray Crystallographic Study⁴ of $[(py)_3Co_3O(OAc)_5(OCH_2CH_2CH_2C_6H_5)][PF_6]$ (7). Large well-shaped brown single crystals of **7** obtained as described above were suitable for X-ray diffraction

Table I. ¹H NMR Data^a

complex (solvent)	¹ H NMR data, δ
3 (CD ₃ CN)	9.29 d (2 H), 8.70 d (4 H), 8.18 t (2 H), 8.33 t (1 H), 7.95 t (2 H), 7.76 t (4 H), 2.19 s (3 H), 2.17 s (6 H), 1.89 s (6 H), 0.73 s (3 H)
4 (CD ₃ CN)	9.20 d (2 H), 8.71 d (4 H), 8.40 t (1 H), 8.29 t (2 H), 8.03 t (2 H), 7.87 t (4 H), 2.25 s (3 H), 2.24 s (6 H), 1.84 s (6 H), 1.03 qt (2 H), 0.13 t (3 H)
5 (CD ₂ Cl ₂)	9.19 d (2 H), 8.65 d (4 H), 8.23 t (1 H), 8.10 t (2 H), 7.88 t (2 H), 7.71 t (4 H), 5.13 m (1 H), 4.43 d (1 H), 4.40 d (1 H), 2.30 s (3 H), 2.23 s (6 H), 1.91 s (6 H), 1.57 d (2 H)
6 (CD ₂ Cl ₂)	9.23 d (2 H), 8.43 d (4 H), 8.25 t (1 H), 7.93 m (4 H), 7.49 t (4 H), 7.04 t (1 H), 6.90 t (2 H), 6.73 d (2 H), 2.34 s (6 H), 2.28 s (3 H), 2.02 s (2 H), 1.94 s (6 H)
7 (CD ₂ Cl ₂)	9.17 d (2 H), 8.62 d (4 H), 8.23 t (1 H), 8.10 t (2 H), 7.87 t (2 H), 7.70 t (4 H), 7.10 m (3 H), 6.71 d (2 H), 2.29 s (3 H), 2.15 s (6 H), 1.97 t (2 H), 1.89 s (6 H), 1.00 t (2 H), 0.92 m (2 H)
8 (CD ₃ CN)	9.24 d (2 H), 8.70 d (4 H), 8.23 t (1 H), 8.19 t (2 H), 7.92 t (2 H), 7.76 t (4 H), 2.25 s (3 H), 2.21 s (6 H), 0.91 t (2 H), 0.52 m (2 H), 0.27 t (3 H)

^a Values for α-hydrogens are in boldface type.

studies. At 20 ± 1 °C, the crystal is monoclinic, with *a* = 35.684 (8) Å, *b* = 9.691 (3) Å, *c* = 27.134 (8) Å, β = 102.74 (2)°, *V* = 9152(5) Å³, and *Z* = 8 [*μ*_a(Mo Kα)⁵ = 1.19 mm⁻¹; *d*_{calc} = 1.459 g cm⁻³]. The space group was uniquely determined by systematically absent reflections as centrosymmetric C₂/c (C_{2h}², No. 15).⁶

Intensity measurements for both compounds were made on a computer-controlled Nicolet autodiffractometer using full (0.90° wide) ω scans and graphite-monochromated Mo Kα radiation for rectangular parallelepiped-shaped specimens having dimensions of 0.40 × 0.60 × 0.62 mm. The crystal was glued to the end of a thin glass fiber having a tip diameter of 0.18 mm and was mounted on a goniometer with its longest edge nearly parallel to the φ axis of the diffractometer. A total of 8385 independent reflections having 3° < 2θ_{Mo Kα} < 50.7° (the equivalent of 0.80 Cu K limiting spheres) were measured with scanning rates of 6, 4, or 2°/min. The data collection and reduction procedures that were used are described elsewhere.⁷

The three crystallographically independent Co atoms and one P atom in the asymmetric unit were located by using (SHELXTL) "direct-methods" techniques. Counter-weighted⁸ full-matrix least-squares refinement of the structure parameters for the three Co and one P atoms gave *R* (unweighted, based on *F*)⁹ = 0.381 for 5402 independent reflections having *I* > 3σ(*I*) and 2θ_{Mo Kα} < 50.7°.

A difference Fourier synthesis based on the model containing three isotropically refined Co atoms and one P atom revealed the remaining 60 non-hydrogen atoms of the respective asymmetric unit. Inclusion of these atoms into the model with the isotropic thermal parameters gave *R*₁ = 0.109 for 5402 reflections. Subsequent counter-weighted cascade block-diagonal least-squares refinement cycles that utilized anisotropic thermal parameters for all non-hydrogen atoms gave *R*₁ = 0.066 for 5402 reflections. Hydrogen atoms H_{41a} and H_{41b} were located from a difference Fourier synthesis and refined as independent isotropic atoms. The five methyl groups (C₂, C₄, C₆, C₈, and C₁₀ and their hydrogens) were refined as rigid rotors with sp³-hybridized geometry and a C–H bond length of 0.96 Å. The initial orientation of each methyl group was determined by difference Fourier positions for the hydrogen atoms. The final orientation of each group was determined by three rotational parameters. The remaining hydrogen atoms were included in the structure factor calculations as idealized atoms (assuming sp² or sp³ hybridization

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- (8) For counter weights: σ_{*r*} = {[σ(*F*_o)]² + (*p*|*F*_o)²}^{1/2} where the "ignorance factor", *p*, has the value of 0.01 in this case.
- (9) The *R* values are defined as *R*₁ = ∑|*F*_o| – |*F*_c|/∑|*F*_o| and *R*₂ = {∑*w*(|*F*_o| – |*F*_c|)²/∑*w*|*F*_o|²}^{1/2}, where *w* (= 1/σ²) is the weight given each reflection. The function minimized is ∑*w*(|*F*_o| – *K*|*F*_c|)², where *K* is the scale factor.

Table II. Atomic Coordinates for Non-Hydrogen Atoms in Crystalline $[(py)_3Co_3O(OAc)_5(OCH_2CH_2CH_2C_6H_5)] [PF_6]^a$

atom type ^b	fract coord			equiv isotropic thermal param, (B), ^c Å ² × 10	atom type ^b	fract coord			equiv isotropic thermal param, (B), ^c Å ² × 10
	10 ⁴ x	10 ⁴ y	10 ⁴ z			10 ⁴ x	10 ⁴ y	10 ⁴ z	
Cation									
Co ₁	3726 (1)	1104 (1)	2358 (1)	46 (1)	C ₉	4675 (2)	171 (5)	1585 (2)	43 (2)
Co ₂	4151 (1)	2368 (1)	1540 (1)	36 (1)	C ₁₀	5079 (2)	-379 (6)	1700 (3)	66 (2)
Co ₃	3874 (1)	-307 (1)	1357 (1)	40 (1)	C ₁₁	3715 (3)	757 (7)	3413 (3)	81 (3)
O _x	3983 (1)	944 (3)	1868 (1)	39 (1)	C ₁₂	3570 (4)	742 (9)	3847 (3)	110 (5)
O _y	3948 (1)	1252 (3)	952 (1)	42 (1)	C ₁₃	3197 (4)	1163 (13)	3817 (4)	133 (6)
O ₁	4166 (1)	1997 (4)	2757 (1)	46 (1)	C ₁₄	2984 (4)	1561 (11)	3365 (4)	121 (5)
O ₂	4365 (1)	3287 (3)	2168 (1)	42 (1)	C ₁₅	3144 (2)	1559 (8)	2944 (3)	82 (3)
O ₃	3252 (1)	321 (4)	2018 (2)	63 (1)	C ₂₁	4595 (2)	3434 (5)	852 (2)	46 (2)
O ₄	3334 (1)	-76 (4)	1229 (1)	53 (1)	C ₂₂	4801 (2)	4358 (6)	634 (2)	53 (2)
O ₅	3917 (1)	-677 (4)	2577 (1)	55 (1)	C ₂₃	4789 (2)	5736 (6)	771 (3)	61 (2)
O ₆	3850 (1)	-1794 (4)	1823 (1)	50 (1)	C ₂₄	4576 (2)	6115 (6)	1103 (2)	55 (2)
O ₇	3498 (1)	2863 (4)	2172 (1)	54 (1)	C ₂₅	4372 (2)	5139 (5)	1300 (2)	45 (2)
O ₈	3702 (1)	3464 (4)	1469 (1)	45 (1)	C ₃₁	3998 (2)	-1508 (6)	436 (2)	57 (2)
O ₉	4631 (1)	1438 (3)	1620 (1)	41 (1)	C ₃₂	3952 (2)	-2376 (7)	30 (2)	79 (3)
O ₁₀	4406 (1)	-729 (3)	1458 (1)	43 (1)	C ₃₃	3683 (3)	-3382 (8)	-22 (3)	92 (3)
N ₁	3502 (2)	1159 (5)	2966 (2)	65 (2)	C ₃₄	3468 (3)	-3492 (8)	330 (3)	94 (4)
N ₂	4386 (1)	3790 (4)	1182 (1)	39 (1)	C ₃₅	3530 (2)	-2594 (6)	731 (2)	66 (2)
N ₃	3792 (1)	-1607 (4)	778 (2)	51 (1)	C ₄₁	3616 (2)	1691 (7)	585 (2)	61 (2)
C ₁	4371 (2)	2902 (5)	2615 (2)	43 (2)	C ₄₂	3716 (3)	2597 (9)	189 (3)	113 (4)
C ₂	4650 (2)	3628 (6)	3022 (2)	54 (2)	C ₄₃	3679 (5)	2258 (11)	-257 (3)	221 (9)
C ₃	3135 (2)	66 (6)	1552 (2)	58 (2)	C ₄₄	3719 (3)	3259 (9)	-674 (3)	99 (4)
C ₄	2711 (2)	-122 (11)	1368 (3)	107 (4)	C ₄₅	3409 (3)	3649 (13)	-1003 (4)	140 (6)
C ₅	3930 (2)	-1706 (6)	2305 (2)	53 (2)	C ₄₆	3429 (3)	4602 (13)	-1379 (4)	121 (5)
C ₆	4062 (3)	-3040 (7)	2585 (3)	84 (3)	C ₄₇	3759 (3)	5160 (9)	-1416 (3)	88 (4)
C ₇	3496 (2)	3588 (6)	1779 (2)	49 (2)	C ₄₈	4077 (3)	4770 (11)	-1081 (3)	121 (5)
C ₈	3206 (2)	4738 (8)	1698 (3)	79 (3)	C ₄₉	4053 (3)	3846 (10)	-710 (3)	113 (4)
Anion I									
P ₁	0 ^e	5000 ^e	0 ^e	82 (1-)	F ₂	-0 (3)	3502 (5)	88 (4)	201 (5)
F ₁	-192 (2)	5166 (7)	446 (2)	159 (3)	F ₃	403 (2)	5123 (11)	336 (3)	199 (4)
Anion II ^d									
P ₂	2475 (2)	4463 (10)	290 (3)	120 (3)	F ₇	2844 (3)	3667 (18)	449 (6)	181 (8)
F ₄	2608 (7)	4696 (37)	-168 (5)	329 (18)	F ₈	2328 (4)	3086 (18)	-16 (8)	174 (9)
F ₅	2108 (4)	5265 (19)	74 (5)	185 (7)	F ₉	2334 (5)	3747 (18)	701 (7)	202 (9)
F ₆	2604 (3)	5884 (17)	612 (4)	157 (6)					

^aThe numbers in parentheses are the estimated standard deviations in the last significant digit. ^bAtoms are labeled in agreement with Figures 1 and S1. ^cThis is one-third of the trace of the orthogonalized B_{ij} tensor. ^dAnion II appears to be statistically disordered between two symmetry-related locations in the lattice. Its atoms were therefore included in all structure factor calculations with occupancies of 0.50. ^eThis is a symmetry-required value and is therefore listed without an estimated standard deviation.

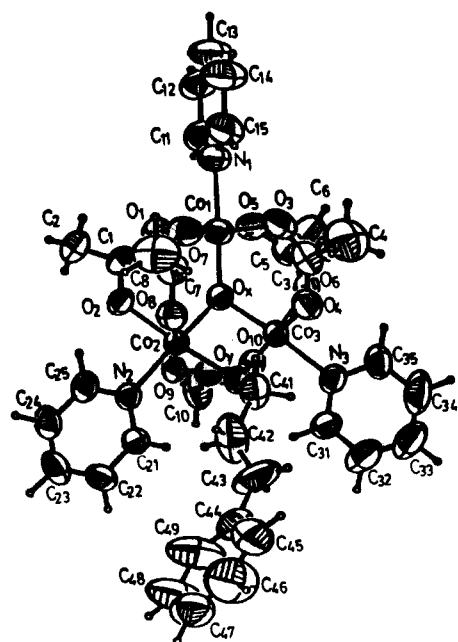


Figure 1. Perspective drawing of the $[(py)_3Co_3O(OAc)_5(OCH_2CH_2CH_2C_6H_5)]^+$ cation in crystalline $[(py)_3Co_3O(OAc)_5(OCH_2CH_2CH_2C_6H_5)][PF_6]$ with non-hydrogen atoms represented by thermal vibration ellipsoids drawn to encompass 50% of their electron density. Hydrogen atoms are represented by arbitrarily small spheres that are in no way representative of their true thermal motion.

of the carbon atoms and a C-H bond length of 0.96 Å) "riding" on their respective carbon atoms. The isotropic thermal parameters of H_{41a} and H_{41b} refined to the final values of 6 (1) and 7 (2) Å², respectively. The isotropic thermal parameter of each remaining hydrogen atom was fixed at 1.2 times the equivalent isotropic thermal parameter of the carbon atom to which it is covalently bonded.

The final structure factor calculations employed a least-squares refinable extinction correction.¹⁰ The final cycles of counter-weighted⁸ cascade block-diagonal least-squares refinement, which employed anisotropic thermal parameters for all non-hydrogen atoms and isotropic thermal parameters for all hydrogen atoms gave $R_1 = 0.054$ and R_2 (weighted, based on F)⁸ = 0.054 for 5402 independent reflections having $2\theta_{MoK\alpha} < 50.7^\circ$ and $I > 3\sigma(I)$.

Structure factor calculations employed recent tabulations of atomic form factors^{5b} and anomalous dispersion corrections^{5c} to the scattering factors of the Co, C₁₁, P, and F atoms. All calculations were performed on a Data General Eclipse S-200 or S-230 computer equipped with 256K of 16-bit words, a floating point processor for 32- and 64-bit arithmetic, and versions of the Nicolet EXTL and SHELXTL interactive crystallographic software packages as modified at Crystallitics Co.

Results and Discussion

The μ -alkoxide complexes $[(py)_3Co_3O(OAc)_5OR][PF_6]$ were synthesized by treatment of $[(py)_3Co_3O(OAc)_6][PF_6]$ (**1**) with an alcohol in refluxing acetonitrile (Scheme I). Complexes where R is methyl, ethyl, propyl, allyl, benzyl, and 3-phenylpropyl were prepared. In a typical procedure, **1** was refluxed for 10 min in a solution comprised of 80% acetonitrile and 20% of the desired alcohol. The complexes can also be prepared from $[(py)_3Co_3O(OAc)_5OH][PF_6]$ **2** in the same manner as from **1**, but the reaction

(10) Larson, A. C. *Acta Crystallog.* **1967**, *23*, 664.

Table III. Bond Lengths in Crystalline $[(py)_3Co_3O(OAc)_5(OCH_2CH_2CH_2C_6H_5)] [PF_6]^a$

type ^b	length, Å	type ^b	length, Å
Co ₁ ...Co ₂	3.194 (1)	Co ₂ ...Co ₃	2.781 (1)
Co ₁ ...Co ₃	3.188 (1)		
Co ₁ -O _x	1.782 (4)	N ₁ -C ₁₁	1.340 (8)
Co ₂ -O _x	1.812 (3)	N ₁ -C ₁₅	1.325 (10)
Co ₃ -O _x	1.818 (3)	C ₁₁ -C ₁₂	1.388 (13)
		C ₁₂ -C ₁₃	1.379 (20)
Co ₂ -O _y	1.933 (3)	C ₁₃ -C ₁₄	1.346 (16)
Co ₃ -O _y	1.921 (3)	C ₁₄ -C ₁₅	1.386 (16)
		N ₂ -C ₂₁	1.331 (7)
Co ₁ -N ₁	1.985 (6)	N ₂ -C ₂₅	1.350 (6)
Co ₂ -N ₂	1.978 (4)	C ₂₁ -C ₂₂	1.373 (9)
Co ₃ -N ₃	1.984 (4)	C ₂₂ -C ₂₃	1.390 (8)
		C ₂₃ -C ₂₄	1.349 (10)
Co ₁ -O ₁	1.907 (3)	C ₂₄ -C ₂₅	1.372 (8)
Co ₁ -O ₃	1.897 (4)		
Co ₁ -O ₅	1.900 (4)	N ₃ -C ₃₁	1.309 (9)
Co ₁ -O ₇	1.909 (4)	N ₃ -C ₃₅	1.324 (8)
		C ₃₁ -C ₃₂	1.368 (9)
Co ₂ -O ₂	1.923 (3)	C ₃₂ -C ₃₃	1.353 (12)
Co ₂ -O ₈	1.896 (4)	C ₃₃ -C ₃₄	1.355 (14)
Co ₂ -O ₉	1.907 (3)	C ₃₄ -C ₃₅	1.372 (10)
Co ₃ -O ₄	1.894 (4)	O _y -C ₄₁	1.433 (7)
Co ₃ -O ₆	1.932 (4)		
Co ₃ -O ₁₀	1.904 (4)	C ₄₁ -C ₄₂	1.490 (11)
		C ₄₂ -C ₄₃	1.233 (12)
O ₁ -C ₁	1.256 (7)	C ₄₃ -C ₄₄	1.52 (1)
O ₂ -C ₁	1.265 (6)	C ₄₄ -C ₄₅	1.32 (1)
O ₃ -C ₃	1.266 (7)	C ₄₄ -C ₄₉	1.34 (2)
O ₄ -C ₃	1.251 (8)	C ₄₅ -C ₄₆	1.39 (2)
		C ₄₆ -C ₄₇	1.32 (2)
O ₅ -C ₅	1.247 (7)	C ₄₇ -C ₄₈	1.34 (1)
O ₆ -C ₅	1.278 (7)	C ₄₈ -C ₄₉	1.37 (1)
		C ₄₁ -H _{41a}	0.95 (5)
O ₇ -C ₇	1.277 (7)	C ₄₁ -H _{41b}	1.10 (6)
O ₈ -C ₇	1.237 (7)		
O ₉ -C ₉	1.245 (6)		
O ₁₀ -C ₉	1.286 (6)		
C ₁ -C ₂	1.490 (7)		
C ₃ -C ₄	1.496 (9)		
C ₅ -C ₆	1.521 (8)		
C ₇ -C ₈	1.506 (9)		
C ₉ -C ₁₀	1.502 (8)		

^aThe numbers in parentheses are the estimated standard deviations in the last significant digit. ^bAtoms are labeled in agreement with Figure 1.

is much slower, or by the addition of "cobaltic acetate" (prepared by the dropwise addition of peracetic acid to a solution of cobaltous acetate) to the desired alcohol followed by the addition of pyridine. The formation of the alkoxide complexes probably involves the dissociation of an acetate ligand followed by the coordination of the alcohol. Attempts to prepare complexes derived from secondary alcohols were unsuccessful, presumably due to steric effects. The compounds were characterized by ¹H NMR, spectroscopy fast-atom-bombardment mass spectroscopy (FAB/MS), and elemental analysis. The 3-phenylpropoxide complex (7) was characterized by X-ray crystallographic techniques.

Characteristic of the μ -alkoxide complexes is the unusually high-field chemical shift of the hydrogen atoms α to the bridging oxygen atom. The chemical shift of the hydrogen atoms α to the μ -oxygen atom is usually about 3 ppm upfield from the chemical shift observed in the uncomplexed alcohol. For example, the chemical shift of the methyl hydrogens in the μ -methoxide complex (3) is 0.7 ppm, compared to a chemical shift of 3.3 for methanol. This phenomenon was observed for all of the complexes reported here. The ¹H NMR data for complexes 3-8 are listed in Table I. The reason for the high-field chemical shift is unclear, but it may be due to the relationship of the μ -alkoxide hydrogens to the cobalt-oxygen bonds.

The μ -alkoxide complexes react with acetic acid, resulting in the displacement of the alkoxide ligand by an acetate to produce

Table IV. Cation Bond Angles in Crystalline $[(py)_3Co_3O(OAc)_5(OCH_2CH_2CH_2C_6H_5)] [PF_6]^a$

type ^b	angle, deg	type ^b	angle, deg
O _x Co ₁ O ₁	88.2 (2)	O ₃ Co ₁ O ₇	86.8 (2)
O _x Co ₁ O ₃	98.7 (2)	O ₅ Co ₁ O ₇	174.6 (2)
O _x Co ₁ O ₅	87.0 (2)	O _x Co ₁ N ₁	172.2 (2)
O _x Co ₁ O ₇	98.0 (2)	O ₁ Co ₁ N ₁	87.0 (2)
O ₁ Co ₁ O ₃	172.6 (2)	O ₃ Co ₁ N ₁	86.3 (2)
O ₁ Co ₁ O ₅	92.4 (2)	O ₅ Co ₁ N ₁	87.0 (2)
O ₁ Co ₁ O ₇	89.7 (2)	O ₇ Co ₁ N ₁	88.2 (2)
O ₃ Co ₁ O ₅	90.5 (2)		
O _x Co ₂ O _y	82.8 (1)	O _y Co ₂ N ₂	96.0 (2)
O _x Co ₂ O ₂	91.6 (1)	O ₂ Co ₂ N ₂	89.1 (2)
O _x Co ₂ O ₈	96.5 (2)	O ₈ Co ₂ N ₂	90.0 (2)
O _x Co ₂ O ₉	88.3 (2)	O ₉ Co ₂ N ₂	85.2 (2)
O _y Co ₂ O ₂	173.5 (1)	Co ₃ Co ₂ O _x	40.1 (1)
O _y Co ₂ O ₈	94.3 (1)	Co ₃ Co ₂ O _y	43.7 (1)
O _y Co ₂ O ₉	89.6 (1)	Co ₃ Co ₂ O ₂	130.3 (1)
O ₂ Co ₂ O ₈	89.6 (1)	Co ₃ Co ₂ O ₈	104.2 (1)
O ₂ Co ₂ O ₉	87.0 (1)	Co ₃ Co ₂ O ₉	81.6 (1)
O ₈ Co ₂ O ₉	174.2 (1)	Co ₃ Co ₂ N ₂	137.2 (1)
O _x Co ₂ N ₂	173.4 (2)		
O _x Co ₃ O _y	83.0 (1)	O _y Co ₃ N ₃	93.5 (2)
O _x Co ₃ O ₄	95.7 (2)	O ₄ Co ₃ N ₃	87.9 (2)
O _x Co ₃ O ₆	91.8 (1)	O ₆ Co ₃ N ₃	91.4 (2)
O _x Co ₃ O ₁₀	89.6 (2)	O ₁₀ Co ₃ N ₃	86.9 (2)
O _y Co ₃ O ₄	93.7 (2)	Co ₂ Co ₃ O _x	39.9 (1)
O _y Co ₃ O ₆	173.2 (1)	Co ₂ Co ₃ O _y	44.0 (1)
O _y Co ₃ O ₁₀	89.5 (2)	Co ₂ Co ₃ O ₄	103.3 (1)
O ₄ Co ₃ O ₆	91.1 (2)	Co ₂ Co ₃ O ₆	130.0 (1)
O ₄ Co ₃ O ₁₀	174.0 (2)	Co ₂ Co ₃ O ₁₀	82.5 (1)
O ₆ Co ₃ O ₁₀	86.1 (2)	Co ₂ Co ₃ N ₃	135.9 (1)
O _x Co ₃ N ₃	175.1 (2)		
Co ₁ O _x Co ₂	125.4 (2)	Co ₂ O _y Co ₃	92.3 (1)
Co ₁ O _x Co ₃	124.6 (2)	Co ₂ O _y C ₄₁	120.6 (3)
Co ₂ O _x Co ₃	100.0 (2)	Co ₃ O _y C ₄₁	115.7 (4)
Co ₁ O ₁ C ₁	127.2 (3)	Co ₃ O ₆ C ₅	126.0 (3)
Co ₂ O ₂ C ₁	129.2 (3)	Co ₁ O ₇ C ₇	129.4 (4)
Co ₁ O ₃ C ₃	128.9 (4)	Co ₂ O ₈ C ₇	126.8 (3)
Co ₃ O ₄ C ₃	126.5 (3)	Co ₂ O ₉ C ₉	125.7 (3)
Co ₁ O ₅ C ₅	126.8 (3)	Co ₃ O ₁₀ C ₉	123.7 (3)
Co ₁ N ₁ C ₁₁	119.4 (5)	O ₁ C ₁ O ₂	127.8 (4)
Co ₁ N ₁ C ₁₅	122.2 (5)	O ₁ C ₁ C ₂	116.1 (5)
C ₁₁ N ₁ C ₁₅	118.3 (7)	O ₂ C ₁ C ₂	116.1 (5)
Co ₂ N ₂ C ₂₁	120.8 (3)	O ₃ C ₃ O ₄	127.5 (5)
Co ₂ N ₂ C ₂₅	121.1 (4)	O ₃ C ₃ C ₄	116.4 (7)
C ₂₁ N ₂ C ₂₅	117.8 (5)	O ₄ C ₃ C ₄	116.1 (6)
Co ₃ N ₃ C ₃₁	120.5 (4)	O ₅ C ₅ O ₆	129.0 (5)
Co ₃ N ₃ C ₃₅	120.9 (4)	O ₅ C ₅ C ₆	115.6 (5)
C ₃₁ N ₃ C ₃₅	118.7 (5)	O ₆ C ₅ C ₆	115.3 (5)
		O ₇ C ₇ O ₈	128.4 (5)
N ₁ C ₁₁ C ₁₂	121.9 (8)	O ₇ C ₇ C ₈	113.9 (6)
C ₁₂ C ₁₂ C ₁₃	118.8 (9)	O ₈ C ₇ C ₈	117.7 (5)
C ₁₂ C ₁₃ C ₁₄	118.9 (12)	O ₉ C ₉ O ₁₀	126.2 (5)
C ₁₃ C ₁₄ C ₁₅	119.9 (12)	O ₉ C ₉ C ₁₀	117.7 (5)
C ₁₄ C ₁₅ N ₁	122.2 (7)	O ₁₀ C ₉ C ₁₀	116.1 (5)
N ₂ C ₂₁ C ₂₂	123.6 (5)	N ₃ C ₃₁ C ₃₂	122.7 (6)
C ₂₁ C ₂₂ C ₂₃	117.4 (6)	C ₃₁ C ₃₂ C ₃₃	118.9 (8)
C ₂₂ C ₂₃ C ₂₄	119.7 (6)	C ₃₂ C ₃₃ C ₃₄	118.9 (7)
C ₂₃ C ₂₄ C ₂₅	119.9 (5)	C ₃₃ C ₃₄ C ₃₅	119.4 (8)
C ₂₄ C ₂₅ N ₂	121.6 (5)	C ₃₄ C ₃₅ N ₃	121.4 (7)
O _y C ₄₁ C ₄₂	112.5 (6)	C ₄₃ C ₄₄ C ₄₅	119 (1)
C ₄₁ C ₄₂ C ₄₃	124.0 (9)	C ₄₃ C ₄₄ C ₄₉	124 (1)
C ₄₂ C ₄₃ C ₄₄	123.6 (10)	C ₄₅ C ₄₄ C ₄₉	117 (1)
		C ₄₄ C ₄₅ C ₄₆	121 (1)
O _y C ₄₁ H _{41a}	107 (3)	C ₄₅ C ₄₆ C ₄₇	121 (1)
O _y C ₄₁ H _{41b}	116 (3)	C ₄₆ C ₄₇ C ₄₈	118 (1)
C ₄₂ C ₄₁ H _{41a}	107 (3)	C ₄₇ C ₄₈ C ₄₉	120 (1)
C ₄₂ C ₄₁ H _{41b}	114 (3)	C ₄₈ C ₄₉ C ₄₄	122 (1)
H _{41a} C ₄₁ H _{41b}	98 (4)		

^aThe numbers in parentheses are the estimated standard deviations in the last significant digit. ^bAtoms are labeled in agreement with Figure 1.

1. This is not surprising in view of the fact that all other Co(III) oxo- and hydroxy-bridged complexes in this series studied in our

laboratory are labile toward ligand substitution and are also structurally interconvertible depending upon the solvent medium.^{2,3} For example, previous studies³ have shown $[(\text{py})_3\text{Co}_3\text{O}(\text{OAc})_3(\text{OH})_2][\text{PF}_6]_2$ (**9**) and $[(\text{py})_4\text{Co}_2(\text{OAc})_3(\text{OH})_2][\text{PF}_6]$ (**10**) to be interconvertible in aqueous acetic acid. Treatment of **9** with ethanol containing 50% by volume acetic acid for 10 min at 120 °C produced the μ -ethoxide complex (**4**). Thus, the μ -alkoxide complexes are also interconvertible with other oxo-centered cobalt complexes, depending upon the solvent medium.

The μ -alkoxide complexes decompose thermally in chlorobenzene at 150 °C to produce a mixture of aldehyde and acetate. For example, the propyl derivative (**8**) gave propionaldehyde (42%) and propyl acetate (13%). The ethyl derivative (**4**) gave mainly ethyl acetate (88%) with some acetaldehyde (~10%), while the 3-phenylpropyl derivative (**7**) produced benzaldehyde (10%) along with 3-phenylpropionaldehyde (48%) and 3-phenylpropyl acetate (5%). The benzyl derivative (**6**) gave benzaldehyde (86%), benzyl acetate (5%), and a small amount of benzoic acid (5%). The aldehydes arise from the oxidation of the alkoxide ligand via a mechanism having the net result of a β -hydride elimination. Cleavage of alcohols coordinated to cobalt(III) is reported to involve both C–C and α -C–H bond cleavage.^{11,13} Aldehydes are a direct product of the α -C–H bond cleavage. The benzaldehyde formed in the decomposition of **7** may be the result of the formation and fragmentation of an aromatic radical cation resulting from the attack of the cobalt cluster on the phenyl ring of the organic ligand. The acetates are presumably the net result of attack of the alkoxide ligand on a coordinated acetate. This could occur by reaction of a dissociated alkoxide ligand or free alcohol with a coordinated acetate or through an intramolecular mechanism requiring no prior dissociation of ligands. In the case of the benzyloxy complex (**6**), essentially the same yields of products were obtained upon reaction of benzyl alcohol with **1** or **2** as were obtained upon thermal decomposition of **6**. The similar selectivity for benzyl acetate suggests a common intermediate for all three reactions. It should be pointed out that anhydrous cobaltous acetate reacts with benzyl alcohol under similar conditions to give benzyl acetate.

Solid State Structure of $[(\text{py})_3\text{Co}_3\text{O}(\text{OAc})_5(\text{OCH}_2\text{CH}_2\text{CH}_2\text{C}_6\text{H}_5)][\text{PF}_6]$ (7**).** The 3-phenylpropoxide complex (**7**) was characterized by a single-crystal X-ray diffraction study that definitively shows discrete $[(\text{py})_3\text{Co}_3\text{O}(\text{OAc})_5$

$(\text{OCH}_2\text{CH}_2\text{CH}_2\text{C}_6\text{H}_5)]^+$ cations (Figure 1) and $[\text{PF}_6]^-$ anions (supplementary Figure S1).¹¹ Final atomic coordinates for non-hydrogen atoms are listed with estimated standard deviations in Table II. Anisotropic thermal parameters for nonhydrogen atoms are given in supplementary Table SI; atomic coordinates for hydrogen atoms are given in supplementary Table SII. Bond lengths and angles for the cation are given with standard deviations in Tables III and IV. Bond lengths and angles for the $[\text{PF}_6]^-$ anion are given in supplementary Table SIII. Listings of the final observed and calculated structure factors are given in supplementary Table SIV. Chemical shifts of the $^{13}\text{C}\{^1\text{H}\}$ NMR signals for $[(\text{py})_3\text{Co}_3\text{O}(\text{OAc})_5\text{OR}][\text{PF}_6]$ complexes in CD_3CN are given in supplementary Table SV.

As shown in the ORTEP drawing, Figure 1, the cation **7**⁺ is an oxo-centered cobalt cluster that is composed of three slightly distorted Co(III) octahedral centers arranged in a triangle with a 3-phenylpropoxy group bridging two of the cobalt atoms (Co_2 and Co_3). Two of the metal–metal distances are similar [3.194 (1) and 3.188 (1) Å]. The remaining metal–metal distance (Co_2 – Co_3) is contracted [2.781 (1) Å] due to the presence of the alkoxide bridge. The central oxygen atom is almost equidistant [1.782 (4), 1.812 (3), and 1.818 (3) Å] from the three cobalt ions and is displaced by 0.33 Å below the least-squares mean plane of the three cobalt ions. The cation contains five bidentate acetate anions that bridge pairs of the cobalt ions. Each metal–metal distance is bridged by two acetate ligands except Co_2 – Co_3 , which has one acetate and one alkoxide bridge. One pyridine is also coordinated to each cobalt ion trans to the common μ_3 -oxygen (O_x). The structure of **7** is almost identical with that reported earlier for $[(\text{py})_3\text{Co}_3\text{O}(\text{OAc})_5\text{OH}][(\text{py})\text{CoBr}_3]$.^{2a} The ^1H and ^{13}C NMR and fast-atom-bombardment mass spectra of **3**–**7** are consistent with the oxo-centered, solid-state structure.

Conclusions

We have reported the synthesis of a family of μ -alkoxy, oxo-centered cobalt(III) complexes. We believe the synthesis of these complexes is general and can be successfully applied to a number of primary alcohols. The μ -alkoxy complexes are structurally related to previously reported oxo-centered cobalt(III) complexes and possess similar reactivity. The complexes thermally decompose to produce a mixture of the aldehyde and the acetate corresponding to the μ -alkoxy ligand, thus making these complexes of interest as models for the transition-metal-mediated oxidation of alcohols.

Supplementary Material Available: A crystal structure report for **7**, listings of anisotropic thermal parameters (Table SI), fractional atomic coordinates for hydrogen atoms (Table SII), and bond lengths and bond angles for anion non-hydrogen atoms (Table SIII) for **7** and chemical shifts (ppm) of $^{13}\text{C}\{^1\text{H}\}$ NMR signals of $[(\text{py})_3\text{Co}_3\text{O}(\text{OAc})_5\text{OR}][\text{PF}_6]$ complexes in CD_3CN (Table SV), and ORTEP drawings of anion molecules for **7** (Figure S1) (14 pages); a listing of observed and calculated structure factors for **7** (Table SIV) (24 pages). Ordering information is given on any current masthead page.

- (11) Hoare, D. G.; Waters, W. A. *J. Chem. Soc.* **1962**, 965 and references therein.
 (12) The preparation of pure "cobaltic acetate" that is not amine stabilized is reported by others and also found in our laboratory to be very irreproducible.² Although we have evidence that the bulk of "cobaltic acetate" consists of $[\text{HOAc}]_x(\text{H}_2\text{O})_{3-x}\text{Co}_3(\text{OAc})_6[\text{OAc}]$ and $[(\text{HOAc})_x(\text{H}_2\text{O})_{3-x}\text{Co}_3(\text{OAc})_5\text{OH}][\text{OAc}]$, other Co(II) and Co(III) complexes are contaminants. Attempts to totally purify the complex, except by addition of amines such as pyridine, have failed to date.
 (13) Hoare, D. G.; Waters, W. A. *J. Chem. Soc.* **1964**, 2560.