

Table II. Rate Constants and Activation Parameters for Inversion Reaction of Λ -[Co(-)-(pedtc)₃]

	CH ₂ Cl ₂	CS ₂
$k_{10^\circ\text{C}}$, s ⁻¹	3.8×10^{-5}	1.5×10^{-5}
$k_{25^\circ\text{C}}$, s ⁻¹	2.1×10^{-4}	8.5×10^{-5}
$k_{40^\circ\text{C}}$, s ⁻¹	1.1×10^{-3}	4.4×10^{-4}
ΔG^\ddagger , kcal/mol	22.0	22.2
ΔH^\ddagger , kcal/mol	19.2	19.0
ΔS^\ddagger , eu	-9.4	-10.6

ligands around the metal and this will be of opposite sense for the two species. There will also be a contribution due to the optical activity of the ligands themselves and this contribution would be expected to be of the same sense in both diastereoisomers. Thus, for one diastereoisomer, the two effects will be additive and lead to a large CD while for the other, the effects will partially cancel, leading to diminished CD. This can be seen in Figure 2. For Λ -[Co(-)-(pedtc)₃], positive CD contributions from both effects appear to exist while the Δ isomer shows a diminished effect due to a negative contribution from the overall configuration but a positive contribution from the ligands.

Molecular models reveal an interesting feature for these complexes. Because of the long flexible tail, a minimum of steric interaction exists only when the tails of all three ligands are wrapped around the molecule in the same sense. As shown in Figure 1, where the (-)-pedtc is depicted, this necessarily gives rise to a C₃ axis in the molecule. It can be seen that the tails are arranged with right-handed chirality in both the Λ and Δ configurations. Thus regardless of the principal chirality associated with the arrangement of the chelate rings about the metal, there is a secondary sphere of atoms with one particular chirality. Thus the stereochemical bias found during synthesis and on standing in solution might be attributed to this feature.

Kinetic data and activation parameters were obtained for the inversion reactions in both methylene chloride and carbon disulfide and are shown in Table II. The activation parameters are similar to values previously reported¹ for the tris(*N,N*-dibenzylthiocarbamato)cobalt(III) complex which was studied by NMR. In all cases, high ΔG^\ddagger and ΔH^\ddagger were found, thus leading to a slow rate of inversion. Inversion in these complexes is usually thought to occur by the trigonal twist or Bailar twist mechanism. Because of the planarity of the chelate rings, the overall complex is slightly twisted and this twist permits easier access to the symmetrical trigonal prismatic transition state. The cobalt(III) complex would be expected to show a twist similar to that found in the tris-

(*N,N*-diethylthiocarbamato)cobalt(III) complex.^{10,11} Here X-ray data showed distortions which would favor formation of the trigonal-prismatic intermediate. The higher activation energy for the cobalt(III) complexes relative to other transition metals has been attributed to ligand field effects. Calculations relating ligand field stabilization energies for octahedral and trigonal-prismatic environments^{12,13} have shown that the greatest barrier to an octahedral-trigonal-prismatic conversion should occur for d⁶ low-spin complexes such as cobalt(III).

The cobalt(III) complexes described here differ from those previously studied in that the dithiocarbamate is only monosubstituted. Earlier studies have dealt with a variety of disubstituted dithiocarbamates where the ligands were not optically active and could give rise to enantiomeric forms only. Hence only dynamic interconversion of the two forms was observed. With the optically active center on the ligand, diastereoisomerism was possible and led to inversion to one specific isomer. The extent and speed of this inversion was very strongly dependent on the solvent chosen. With oxygenated solvents such as alcohols or ketones, very slow changes occurred. This could possibly be attributed to interaction between the oxygen of the solvent and the N-H bonds of the ligands. No such solvent dependency was noted for complexes containing disubstituted ligands. Thus, these solvent interactions could hinder the approach to the transition state. Nonpolar or weakly polar solvents would not show this type of interaction and inversion could occur more readily as was observed in our studies.

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Synthesis of Transition-Metal Carboxylato Complexes^{1,2}

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The preparations in high yields of (carboxylato)pentaamminecobalt(III) complexes from hydroxopentaamminecobalt(III) by reaction with carboxylic acid anhydrides and *p*-nitrophenyl and 2,4-dinitrophenyl esters are described. The stereospecific synthesis of *cis*- and *trans*-bis(acetato) complexes from *cis*- and *trans*-diaquabis(ethylenediamine)cobalt(III), respectively, has been accomplished. The acylation reactions have been extended to the preparation of the (acetato)pentaammine complexes of Cr(III), Rh(III), and Ru(III). The solvolysis in DMF of aquapentaamminecobalt(III) induced by acetyl trifluoromethanesulfonate has been shown to proceed by a mechanism which involves retention of the oxygen atom of the aqua ligand.

Introduction

Carboxylato complexes of transition metals, especially pentaammine(carboxylato)cobalt(III) salts, have been widely investigated in recent years. In particular, Taube, Gould, and

their co-workers have examined the electron-transfer reactions of such systems.^{4,5} Other workers have studied the photolysis of carboxylato complexes as sources of organic free radicals.⁶ It has also been shown that other groups, such as α carbonyl

present in the carboxylato ligand, retain their expected chemical reactivity⁷ offering the possibility of elaborating more complex structures. There is, therefore, an interest in developing synthetic methods for preparing carboxylato complexes, particularly if they are reasonably general and involve mild conditions.

The most used method to date has been the anation of aqua complexes. This reaction, which appears to have been used first by Gibbs and Genth⁸ in 1857, has been widely employed by Taube and Gould for the preparation of pentaammine-(carboxylato)cobalt(III) salts.⁴ These latter workers have developed useful improvements involving the anation of dimethylformamido complexes in dimethylformamide (DMF),^{4b} the aqua complex in ethylene glycol,^{4h,8} and the carbonato complex in diglyme^{4d} or methanol.⁴ⁱ These methods have considerable generality, but failures have been documented and contamination of the complexes by the parent acid has often been encountered. Silver ion catalyzed anation reactions have been reported^{9,10} but not exploited.

The anation reaction is clearly unsuitable in cases where preservation of the stereochemistry of the central metal atom, retention of label in ¹⁸O aqua complexes, or regiospecific introduction of ambident anions such as thiol or thione carboxylates is desired. A reaction which conceivably does not suffer from these disadvantages and which offers the possibility of mild conditions, high yields, and reasonable generality is the direct acylation of the hydroxo ligand. Although Werner¹¹ in 1907 described the successful conversion of hydroxopentaamminecobalt(III) nitrate to the acetato and propionate complexes by trituration with the corresponding acid anhydrides, the only other reported use of this method prior to our preliminary communication³ was the preparation of (acetato)pentaamminecobalt(III).¹² We now report details of experiments which we believe give high yields under mild conditions in all cases in which the corresponding acid anhydrides or related acylating reagents are available, provided, of course, the hydroxo ligand is reasonably nucleophilic.

Experimental Section

General Procedures. Compounds were characterized by using standard spectral techniques and elemental analysis. Proton NMR spectra were recorded with either Varian A-60A or HA-100 spectrometers with samples in D₂O or Me₂SO-*d*₆; sodium 4,4-dimethyl-4-silapentane-1-sulfonate or tetramethylsilane was used as an internal standard. ¹³C NMR spectra were recorded, by using a CFT-20 spectrometer, for Me₂SO-*d*₆ solutions with Me₄Si as an internal reference. KBr disks or Nujol mulls were used in recording IR spectra on a Perkin-Elmer 137 Infracord spectrophotometer. Visible spectra were recorded on a Cary 14 spectrophotometer and were consistent with literature values of known carboxylato complexes.^{4a} Melting points were taken on a Thomas-Hoover capillary melting point apparatus and were uncorrected. C, H, and N elemental analyses were performed by Midwest Microlab Inc. or the Micro-analytical Section, C.S.I.R.O., Melbourne, Australia. Cobalt analyses were performed spectrophotometrically by the method of Taube.^{4a} Nitrogen analyses for ammine ligands were carried out for some complexes by decomposing them in 2 N sodium hydroxide and estimating the ammonia produced with the method of Elvidge and Sammes.¹³ Chromium analyses were carried out by the method of Baltisberger and King.¹⁴

Organic solvents were distilled before use and dried over Linde type 4A molecular sieves. For reactions involving acylium ions, the solvents were distilled from CaH₂ and stored over molecular sieves. All other chemicals used were of reagent grade or prepared by literature methods unless otherwise noted.

Aquapentaamminecobalt(III) Trifluoromethanesulfonate. This was prepared by treating a hot aqueous solution of the aquapentaammine tribromide¹⁵ with a slight excess of silver trifluoromethanesulfonate, filtering to remove silver bromide, and evaporating to dryness under reduced pressure. The complex was isolated as the trihydrate. Purification by dissolution in absolute ethanol, filtration, and re-

precipitation with diethyl ether remove the water of hydration. A typical yield was 87%.

Anal. Calcd for C₃H₁₇CoF₉N₅O₁₃S₃: C, 5.91; H, 2.81; N, 11.49. Found: C, 6.13; H, 2.99; N, 11.19.

(Acetato)pentaamminecobalt(III) Perchlorate. This salt was prepared by several methods.

(i) From Acetic Anhydride in DMF. Aquapentaamminecobalt(III) perchlorate (92 mg, 2 × 10⁻⁴ mol) in DMF (2 mL) was treated with *N,N*-dimethylbenzylamine (DMB) (0.059 mL, 4 × 10⁻⁴ mol) and then acetic anhydride (0.057 mL, 6 × 10⁻⁴ mol). The solvent was removed by rotary evaporation at 25 °C (1 mm) to yield an oil. Addition of water (3 mL) and reevaporation afforded a microcrystalline pink solid which on trituration with absolute ethanol (3 × 3 mL) followed by diethyl ether (3 × 3 mL) and drying overnight at 25 °C (1 mm) gave the acetato complex (80 mg, 99%). The proton NMR spectrum showed only absorptions ascribable to the (acetato)pentaammine.

(ii) From Acetic Anhydride in Water. Treatment of the aqua complex (230 mg, 5 × 10⁻⁴ mol) in water (2.4 mL) with ammonia (3 × 10⁻³ mol) and acetic anhydride (1.5 × 10⁻³ mol) yielded the acetato perchlorate (186 mg, 93%) on cooling and addition of ethanol and diethyl ether (1:1, 6 mL).

(iii) From *p*-Nitrophenyl Acetate. The aqua complex (138 mg, 3 × 10⁻⁴ mol) and DMB (2.1 × 10⁻³ mol) in DMF (2 mL) were treated with *p*-nitrophenyl acetate (163 mg, 9 × 10⁻⁴ mol) in DMF (1 mL). After 1 h, water (15 mL) was added, causing precipitation of a yellow solid which was removed by ether extraction (2 × 20 mL). The solution was acidified with HClO₄, extracted again, and evaporated to dryness. Trituration with ethanol (3 × 3 mL) and ether (3 × 3 mL) yielded the product (121 mg, 98%) which was pure by NMR.

(iv) From Acetyl Perchlorate. Acetyl chloride (47 mg, 6 × 10⁻⁴ mol) was added to anhydrous silver perchlorate (137 mg, 6.6 × 10⁻⁴ mol) in DMF (2 mL). This solution was added in one portion to the aqua complex (92 mg, 2 × 10⁻⁴ mol) and DMB (0.02 mL, 1.4 × 10⁻³ mol) in DMF (2 mL). Workup as described in (i) afforded the product (97%) which was pure by NMR.

(Acetato)pentaamminecobalt(III) Trifluoromethanesulfonate. Aquapentaamminecobalt(III) trifluoromethanesulfonate (0.25 g, 4.1 × 10⁻⁴ mol) was dissolved in DMF (2 mL) and treated with *N,N*-dimethylbenzylamine (0.20 mL, 1.4 × 10⁻³ mol) and acetic anhydride (0.12 mL, 1.2 × 10⁻³ mol). The solution was evaporated to an oil under reduced pressure and treated with water (5 × 10 mL) followed by evaporation after each addition. The resulting oil was dissolved in acetone-ethanol (2:1), and the salt was precipitated by the slow addition of ether. The product was washed with ethyl acetate (3 × 10 mL) and ether (3 × 10 mL) to afford the pure salt (0.17 g, 84%).

Anal. Calcd for C₄H₁₈CoF₆N₅O₈S₂: C, 9.58; H, 3.62; Co, 11.8; N, 13.97. Found: C, 9.83; H, 3.93; Co, 11.5; N, 13.72.

(*p*-Benzoylbenzoato)pentaamminecobalt(III) Perchlorate. This preparation is typical of those in which the acid anhydride is generated in situ.

To dicyclohexylcarbodiimide (0.82 g, 3.95 × 10⁻³ mol) in DMF (8 mL) was added *p*-benzoylbenzoic acid (2.1 g, 9.21 × 10⁻³ mol) in DMF (3 mL). This solution was stirred for 1 h to allow complete formation of the anhydride. Precipitation of dicyclohexylurea occurred. To this mixture was added a solution of aquapentaamminecobalt(III) perchlorate (0.62 g, 1.35 × 10⁻³ mol) and DMB (1.52 mL, 1.02 × 10⁻² mol) in DMF (5 mL). The reaction was allowed to proceed for 15 min and was then cooled in an ice bath for 15 min to precipitate as much of the urea as possible. Filtration and evaporation at reduced pressure in a rotary evaporator yielded an oil which was treated with water (3 × 15 mL) followed by evaporation after each addition. Ethanol (25 mL) was added to the oily product to affect precipitation of the complex which was removed by filtration. Addition of ether to the filtrate afforded a second crop of precipitate. The combined precipitate was purified by washing with ethanol-ether (1:1, 3 × 10 mL) and ether (3 × 10 mL) followed by recrystallization from 0.05 M perchloric acid. (*p*-Benzoylbenzoato)pentaamminecobalt(III) perchlorate (0.63 g, 95%) was characterized by its ¹³C spectrum (Me₂SO-*d*₆) which showed only the expected ten absorptions (δ 128.6, 128.8, 128.9, 129.5, 132.9, 136.8, 138.7, 138.8, 174.0, 195.6).

(*p*-Formylbenzoato)pentaamminecobalt(III) Perchlorate. Aquapentaamminecobalt(III) perchlorate (1.0 g, 2.17 × 10⁻³ mol) and *p*-formylbenzoic acid (2.28 g, 1.52 × 10⁻² mol) were reacted and worked up as described in the previous experiment. (*p*-Formylbenzoato)pentaamminecobalt(III) perchlorate monohydrate was obtained as red needles and had the expected ¹³C NMR spectrum

(δ 128.8, 129.4, 137.5, 140.4, 173.9, 193.0).

***o*-Benzoylbenzoic Anhydride.** *o*-Benzoylbenzoic acid (4.0 g, 1.77×10^{-2} mol) was added to a magnetically stirred solution of dicyclohexylcarbodiimide (1.82 g, 8.8×10^{-3} mol) in freshly distilled dry ether (30 mL). Stirring was continued for 1 h after which the mixture was cooled to 0 °C for 15 min. The solid which separated was removed by filtration and extracted with cold ethyl acetate (4 \times 25 mL) and then with hot (70 °C) ethyl acetate (2 \times 25 mL). Petroleum ether was slowly added to the combined washings until they became turbid, and the mixture was stored in a refrigerator overnight. *o*-Benzoylbenzoic anhydride was recovered by filtration as fine colorless crystals (2.89 g, 75%), mp 110–111 °C, which had the expected 12-line ^{13}C NMR spectrum (δ 127.1, 127.9, 128.4, 129.4, 129.6, 130.9, 133.25, 133.5, 136.2, 142.4, 160.5, 195.2). In contrast, an authentic sample of 1-phenyl-1-(*o*-benzoylbenzoxy)phthalide generously provided by Dr. M. S. Newman, exhibited a spectrum with 27 peaks (1 overlap) with characteristic absorptions at δ 163.1, 167.3, 196.0 (C=O), and 105.6 (sp^3 carbon bearing two oxygen atoms).

Anal. Calcd for $\text{C}_{28}\text{H}_{18}\text{O}_5$: C, 77.41; H, 4.18. Found: C, 77.27; H, 4.26.

(*o*-Benzoylbenzoato)pentaamminecobalt(III) Perchlorate. This preparation is typical of those in which the previously prepared acid anhydride is employed.

To a solution of aquapentaamminecobalt(III) perchlorate (0.44 g, 9.5×10^{-4} mol) in DMF (5 mL) was added DMB (0.83 mL, 5.67×10^{-3} mol) and *o*-benzoylbenzoic anhydride (1.23 g, 2.84×10^{-3} mol) in DMF (4 mL). After 10 min, ethanol (5 mL) and ether (200 mL) were added. A red oil separated from which the solvent was separated by decantation. The oil was dissolved in ethanol–acetone (1:1, 30 mL). The addition of ether (200 mL) afforded a pink microcrystalline powder which was washed successively with absolute ethanol (5 \times 10 mL) and ether (5 \times 10 mL). The air-dried product (0.49 g, 91%) had the expected ^{13}C NMR spectrum ($\text{Me}_2\text{SO}-d_6$) (δ 197.5, 173.9, 140.6, 137.0, 133.9, 133.0, 130.7, 130.4, 129.0, 128.9, 128.8, 123.0).

Bis(2,4-dinitrophenyl) Fumarate. Finely ground anhydrous sodium 2,4-dinitrophenylate¹⁶ (16.5 g, 8.0×10^{-2} mol) and freshly distilled fumaryl chloride (6.0 g, 3.92×10^{-2} mol) were added to chloroform (70 mL), and the mixture was refluxed for 1 h. The reaction mixture was cooled to 0 °C and the solid residue removed by filtration. The residue was taken up in dry acetone (400 mL) and filtered hot to remove sodium chloride. Removal of the solvent and recrystallization of the residue from acetone afforded pure bis(2,4-dinitrophenyl) fumarate (10.7 g, 61%, mp 198–199.5 °C).

Anal. Calcd for $\text{C}_{16}\text{H}_8\text{N}_4\text{O}_{12}$: C, 42.9; H, 1.8; N, 12.5; O, 42.9. Found: C, 42.7; H, 1.8; N, 12.4; O, 42.7.

Decaammine-(μ -fumarato)-dicobalt(III) Perchlorate. Bis(2,4-dinitrophenyl) fumarate (0.5 g, 1.11×10^{-3} mol) and aquapentaamminecobalt(III) perchlorate (1.03 g, 2.24×10^{-3} mol) were dissolved in DMF (25 mL), and DMB (0.91 g, 6.7×10^{-3} mol) was added. The solution was shaken for 5 min and the complex was then precipitated by the addition of ethanol (25 mL) followed by ether (50 mL). The precipitate was removed by filtration, washed successively with ethanol and ether, and recrystallized from hot (70 °C) 0.02 N perchloric acid to yield the pure μ -fumarato complex (0.77 g, 87%).

***cis*-Diaquabis(ethylenediamine)cobalt(III) Nitrate.** This complex was prepared by a modification of the method described by Tong and Yankwich.¹⁷

***cis*-Dichlorobis(ethylenediamine)cobalt(III) chloride¹⁸** (2.0 g, 7.0×10^{-3} mol) was treated at 0 °C with water (3 mL) and silver oxide (2.5 g, 1.1×10^{-2} mol). The mixture was filtered and the residue washed with water (5 mL). The combined filtrate and washings were adjusted to pH 4 with concentrated nitric acid and allowed to equilibrate for 1 day in the presence of decolorizing charcoal as a catalyst.¹⁹ The solution was cooled to 0 °C and the *cis* complex was precipitated as salmon pink crystals by the slow addition of ice-cold ethanol. The crystals were removed by filtration, washed with absolute ethanol and ether, and dried under vacuum. The product (1.71 g, 61%) had the proton NMR spectrum expected for the *cis* isomer.

***cis*-Bis(acetato)bis(ethylenediamine)cobalt(III) Acetate.** *cis*-Diaquabis(ethylenediamine)cobalt(III) nitrate (0.5 g, 1.25×10^{-3} mol) was dissolved in DMF (15 mL). Acetic anhydride (0.5 g, 5.0×10^{-3} mol) and then DMB (0.6 g, 4.5×10^{-3} mol) were added, and the mixture was vigorously shaken for 5 min. The slow addition of ethyl acetate to the mixture caused precipitation of pink crystals which were removed by filtration and washed with ether. The product was dissolved in the minimum quantity of absolute ethanol and precipitated

by the slow addition of ethyl acetate. Repetition of this procedure followed by drying under vacuum afforded *cis*-bis(acetato)bis(ethylenediamine)cobalt(III) acetate (2.7 g, 61%). The proton NMR spectrum (D_2O) exhibited the following absorptions: δ 1.85 (3 H, s, CH_3COO), 1.95 (6 H, s, CH_3COOCO), 2.49 (4 H, bs, CH_2 trans to OAc), 2.75 (4 H, bs, CH_2 cis to OAc), 5.80 (bs, *cis* NH_2). The trans NH_2 absorption is not observed because exchange with deuterium of the solvent is rapid.

Anal. Calcd for $\text{C}_7\text{H}_{15}\text{CoN}_4\text{O}_4$: Co, 16.56. Found: Co, 16.47.

***trans*-Diaquabis(ethylenediamine)cobalt(III) Dinitrate.** *trans*-Diaquabis(ethylenediamine)cobalt(III) nitrate was prepared by a modification of the method of Tong and Yankwich.¹⁷ *trans*-Dichlorobis(ethylenediamine)cobalt(III) chloride¹⁸ (2.0 g, 1×10^{-3} mol) was treated at 0 °C with water (3 mL) and silver oxide (2.5 g, 1.1×10^{-3} mol). The mixture was filtered and the residue of silver chloride washed with water. The basic filtrate was allowed to equilibrate for 1 week. The solution was then filtered and acidified with concentrated nitric acid (10 mL). Ethanol (20 mL) was added and the less soluble *trans*-diaqua nitrate was isolated by partial precipitation at 0 °C with the addition of ether. The tan crystals were removed by filtration, washed with ethanol and ether, and dried under vacuum. The product (1.12 g, 40%) was shown by proton NMR to be stereochemically pure.

***trans*-Bis(acetato)bis(ethylenediamine)cobalt(III) Nitrate.** *trans*-Diaquabis(ethylenediamine)cobalt(III) nitrate (0.5 g, 1.25×10^{-3} mol) was dissolved in DMF (15 mL). Acetic anhydride (0.5 g, 5×10^{-3} mol) was added to the solution followed by DMB (0.6 g, 4.5×10^{-3} mol). The solution was shaken vigorously for 5 min. The *trans*-bis(acetato) nitrate was precipitated from solution by the slow addition of ether with stirring, recovered by filtration, and washed with ethanol and ether. Purification was accomplished by dissolution in DMF and reprecipitation by ether. The crystals were recovered by filtration, washed with ethanol and ether, and vacuum-dried. This procedure afforded pure *trans*-bis(acetato)bis(ethylenediamine)cobalt(III) nitrate (0.39 g, 87%). The proton NMR spectrum (D_2O) exhibited the following absorptions: δ 1.72 (6 H, s, CH_3COOCO), 2.70 (8 H, m, CH_2), and 5.61 (b, NH_2).

Anal. Calcd for $\text{C}_8\text{H}_{22}\text{CoN}_5\text{O}_7$: Co, 16.41. Found: Co, 16.40.

In a similar preparation in which the acetic anhydride was replaced by 2,4-dinitrophenyl acetate,¹⁶ there was an immediate color change on the addition of DMB, and the *trans*-bis(acetate) was recovered in theoretical yield.

Aquapentaamminechromium(III) Perchlorate. Finely ground aquapentaamminechromium(III) nitrate³⁹ (20.0 g, 7.6×10^{-3} mol) was dissolved in water (260 mL). The solution was filtered and cooled to 0 °C. Precipitation of the perchlorate salt was induced by the slow addition of perchloric acid (40 mL) to the stirred solution. Light orange crystals were removed by filtration and washed with absolute ethanol followed by ether. This process was repeated twice to yield the pure perchlorate (26.6 g, 82%).

Anal. Calcd for $[\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}](\text{ClO}_4)_3$: Cr, 11.45. Found: Cr, 11.45.

(Acetato)pentaamminechromium(III) Perchlorate. Aquapentaamminechromium(III) perchlorate (1.0 g, 2.2×10^{-3} mol) was added to a solution of 2,4-dinitrophenyl acetate (0.5 g, 2.2×10^{-3} mol) and *N,N*-dimethylbenzylamine in DMF (20 mL). After 10 min, absolute ethanol (250 mL) was added with stirring followed by ether (500 mL). The pink crystals so obtained were removed by filtration and washed with ethanol and ether. Repetition of the precipitation procedure afforded pure (acetato)pentaamminechromium(III) perchlorate (0.77 g, 88%).

Anal. Calcd for $[\text{Cr}(\text{NH}_3)_5\text{OCOCH}_3](\text{ClO}_4)_2$: Cr, 13.16; N, 14.59. Found: Cr, 13.2; N, 14.6.

(Acetato)pentaamminerhodium(III) Trifluoromethanesulfonate. Aquapentaamminerhodium(III) trifluoromethanesulfonate (prepared from chloropentaamminerhodium(III) dichloride and silver trifluoromethanesulfonate) (0.2 g, 3.1×10^{-4} mol) in DMF (4 mL) was treated with *N,N*-dimethylbenzylamine (0.9 mL, 6.2×10^{-3} mol) and acetic anhydride (0.09 mL, 9.2×10^{-4} mol). The solution was evaporated under reduced pressure and the residue was treated with water (3 \times 5 mL) followed by evaporation after each addition. The pale yellow solid so obtained was dissolved in acetone, reprecipitated by ether, and washed with ethanol (3 \times 10 mL) to yield the pure acetato complex (0.136 g, 81%). The salt had the expected light absorption²¹ and was shown by both ^1H and ^{13}C NMR to be free from acetate ion.

(Acetato)pentaammineruthenium(III) Trifluoromethanesulfonate. Concentrated ammonium hydroxide (0.15 mL, 2.2×10^{-3} mol) was added to chloropentaammineruthenium(III) dichloride (0.065 g, 2.2×10^{-4} mol; prepared from RuCl_3^{22}) in water (3 mL). The solution was heated for approximately 15 min over a steam bath until it was deep red indicating the formation of the hydroxo complex. To this solution was added acetic anhydride (0.21 mL, 2.2×10^{-3} mol) at which time the solution turned brownish yellow. The solution was acidified with 10% aqueous trifluoromethanesulfonic acid (2 mL) and then treated with silver trifluoromethanesulfonate (0.23 g, 8.8×10^{-4} mol). After removal of the silver chloride, the solution was evaporated to dryness. The residue was dissolved in ethyl acetate and precipitated with ether. The precipitate was washed with ethyl acetate (3×10 mL) and ether (3×10 mL) to yield the acetato complex as a white solid (0.08 g, 67%) which had the expected UV spectrum of the (acetato)pentaammineruthenium(III) dication.²³ This spectrum remained unchanged on basification.

(*N,N*-Dimethylformamido)pentaamminecobalt(III) Perchlorate. Aquapentaamminecobalt(III) perchlorate (4.60 g, 1×10^{-2} mol) and silver perchlorate (6.64 g, 3.2×10^{-2} mol) in DMF (25 mL) were treated with acetyl chloride (2.4 g, 3×10^{-2} mol). After removal of the silver chloride, the solution was evaporated to yield a wet solid which was dissolved in water (200 mL). The solution was filtered and reduced to a small volume (50 mL). Ethanol (50 mL) was added and the mixture was stored at -15°C overnight. The dimethylformamido complex was removed by filtration (4.76 g, 93%). The proton spectrum exhibited absorptions at δ 7.41, 2.97, and 3.13 compared with δ 7.90, 2.79, 2.94 for *N,N*-dimethylformamide itself.

Competitive Acetylation of Aqua and Acetato Complexes. Aquapentaamminecobalt(III) perchlorate (46 mg, 10^{-4} mol), (acetato)pentaamminecobalt(III) perchlorate (40 mg, 10^{-4} mol), and silver perchlorate (21 mg, 10^{-4} mol) in DMF (0.5 mL) were treated with acetyl chloride (0.0057 mL, 0.8×10^{-4} mol). After 10 s, the reaction was quenched with water (2 drops) and the mixture was filtered and evaporated to dryness under high vacuum. Analysis of the solid residue was carried out by proton NMR by using a known amount of *tert*-butyl alcohol in D_2O as an integration standard. This showed that no acetato complex had reacted and that the aqua complex had been converted to the *N,N*-dimethylformamido complex.

¹⁸O-Enriched Aquapentaamminecobalt(III) Perchlorate. Aquapentaamminecobalt(III) perchlorate (2.3 g) was dissolved in 1.5% H_2^{18}O (10 mL), and the pH was adjusted to 2.3 with concentrated perchloric acid (0.00042 mL). The solution was stored at 50°C in the dark. After 3.5 days the solution was cooled to 4°C and the crystals (1.60 g), which were removed by filtration, were washed with methanol. The aqueous filtrate was evaporated to dryness to give a further quantity (0.67 g) of the aqua salt.

Isotopic analysis was performed by first converting the triperchlorate to the tribromide and then converting the H_2^{18}O ligand to CO_2 by a modification of the method of Boyer et al.²⁴ The tribromide (100 mg, 2.5×10^{-4} mol) and recrystallized guanidine hydrochloride (8 mg) were sealed in a break-seal ampule and heated to 250°C for 8 h. Thereafter the method of Boyer was followed and the CO_2 was examined mass spectrometrically for the relative abundances of the P and P + 2 ions by using a MS-9 mass spectrometer. A number of measurements were made for each CO_2 sample and the results for duplicate analyses were 1.187 ± 0.003 and 1.21 ± 0.04 .

Reaction of ¹⁸O-Labeled Aqua Complex with Acetyl Trifluoromethanesulfonate. Aqua complex (enriched by $4.432 \pm 0.088\%$ ¹⁸O)²⁶ (0.402 g, 6.6×10^{-4} mol) and silver trifluoromethanesulfonate (0.74 g, 2.76×10^{-3} mol) in DMF (7 mL) were treated with acetyl chloride (0.19 mL, 2.64×10^{-3} mol) with rapid stirring. The solution was then evaporated in a rotary evaporator to a wet solid. Water (5 mL) was added followed by filtration to remove silver chloride. The solution was evaporated to an oil and treated with water (2×5 mL) followed by evaporation after each addition. Addition of ethanol (5 mL) and ether followed by filtration allowed the isolation of a red solid which was dried in vacuo. ¹H NMR showed the complex to be contaminated with free DMF. Treatment with water followed by evaporation after each addition produced a solid which was then dissolved in ethanol-acetone (1:1) and reprecipitated with ether. This procedure was repeated. Washing with ethyl acetate (3×10 mL) and ether (3×10 mL) yielded a solid (0.23 g) which was shown by ¹H NMR to be free of uncomplexed DMF. The solid was then placed in a small test tube equipped with a ground-glass joint and closed with a stopper. The tube was heated in an oil bath at 130°C for 3 h. The liberated

DMF collected in the cooler upper portion of the vessel and was washed into another vessel with ether (1.5 mL). The isotopic enrichment was determined from the increase in the ratio of parent ion intensities (P + 2)/P for the labeled and unlabeled DMF by using gas chromatography/mass spectral techniques.³⁷ It was found to be $4.084 \pm 0.116\%$ ¹⁸O.

Exchange of DMF in (*N,N*-Dimethylformamido)pentaamminecobalt(III) Perchlorate. The *N,N*-dimethylformamido complex (100 mg) was dissolved in DMF-*d*₇ (112 mg) in a 5-mm NMR tube. Me_4Si (2% v/v) provided a lock signal and *p*-xylene (6 mg) was used as an internal intensity standard. The exchange reaction was followed for approximately one half-life by integrating the signals of the formyl proton in free and bound DMF and the aromatic protons of the *p*-xylene.

In experiments under acidic conditions, anhydrous HCl (5 mL, 2.2×10^{-4} mol) was passed into a solution of silver perchlorate (86 mg, 4×10^{-4} mol) in DMF-*d*₇ (228 mg). The supernatant was used to dissolve the *N,N*-dimethylformamido complex (103 mg, 3.2×10^{-4} mol).

Rate constants ($10^{-4}k$, s^{-1}) for exchange are as follows.

temp, °C	neutral	acidic
68	2.3 ± 0.7	1.3 ± 0.1
83.5	5.2 ± 0.8	5.7 ± 0.4

Results and Discussion

Conversion of Hydroxopentaamminecobalt(III) to (Acetato)pentaamminecobalt(III). Werner's original experiments¹¹ involved a heterogeneous reaction of acetic anhydride with solid hydroxopentaamminecobalt(III) nitrate. We have directed our attention solely to reactions in solution. As discussed below, the reactions of acetic anhydride and other acetylating reagents require the presence of the hydroxo rather than the aqua complex. The former may be used directly with 1 equiv of base or may be generated in situ by the addition of 2 equiv of base to the aqua salt according to the stoichiometry in equation 1 (L \equiv NH_3 , B: \equiv base). Dimethylformamide [L_5CoOH_2]³⁺ + 2B: + $\text{CH}_3\text{COX} \rightarrow [\text{L}_5\text{CoO}_2\text{CCH}_3]^{2+} + 2\text{BH}^+ + \text{X}^-$ (1)

(DMF) proved to be a satisfactory solvent for the perchlorate salts of both the aqua and hydroxo complexes. The corresponding trifluoromethanesulfonates²⁵ have very much higher solubilities, whereas salts involving the more common anions such as halides and nitrates are poorly soluble in DMF and indeed in all usual polar aprotic solvents. When the aquapentaammine is used, deprotonation to the hydroxo derivative is conveniently achieved in situ by the addition of *N,N*-dimethylbenzylamine (DMB), the corresponding perchlorate salt of which can readily be separated from the desired product by virtue of its solubility in absolute ethanol.

The reaction of the hydroxo complex under the above conditions is extremely rapid and gives virtually quantitative yields of the acetato complex. Buckingham and Engelhardt²⁶ have studied the kinetics of the analogous reaction for propionic anhydride in aqueous solutions and have confirmed that the process is indeed a rapid one.

Acetyl chloride can also be used but is inconvenient because it may lead to precipitation of mixed chloride salts during the reaction. *p*-Nitrophenyl acetate is also an effective reagent and gives quantitative yields.

The method of choice for the preparation of the acetato perchlorate is the reaction of acetic anhydride and the aquapentaammine salt in aqueous ammonia at room temperature. Under these conditions analytically pure acetato complex is obtained in 93% yield on the addition of ethanol.²⁷

Preparation of Other Carboxylato Complexes. Scope of the Reaction. The facile preparations of (acetato)pentaamminecobalt(III) salts just described have been extended to a variety of carboxylato complexes with similar success (Table I). Some of the examples were chosen because they were cases

Table I. Preparation of (Carboxylato)pentaamminecobalt(III) Perchlorates

ligand	method	yield %	% Co		% N ^a	
			calcd	found	calcd	found
benzoato	anhydride	51	12.7	12.7		
<i>p</i> -acetamidobenzoato	DCC/acid	67	11.3	11.3	16.3	16.3
<i>o</i> -benzoylbenzoato	anhydride	91	10.4	10.3	12.1	11.8
<i>p</i> -benzoylbenzoato	DCC/acid	95	10.4	10.3		
<i>p</i> -formylbenzoato	DCC/acid	72	11.6	11.5	13.7	13.5
<i>p</i> -formylcinnamato ^b	DCC/acid	64	11.4	11.4	16.4	16.4
hydrogen maleato	anhydride	79	12.9	12.8		
isonicotinato ^c	DCC/acid	96				
pivalato	anhydride	66	13.3	12.9		
sorbato	DCC/acid		12.95	12.6		
μ -fumarato ^d	DNPE ^e	87	14.8	14.7	21.25	21.2

^a Nitrogen of ammine ligands only. ^b Monohydrate. ^c Pure by proton NMR. ^d Dicobalt complex. ^e Bis(2,4-dinitrophenyl) ester.

Table II. Chemical Shifts (ppm) of Carbonyl Carbons Atoms in (Carboxylato)pentaamminecobalt(III) Salts in Me₂SO-d₆

ligand	δ_L	δ_A^a	$\delta_L - \delta_A$
acetato	180.9	172.1	8.8
<i>p</i> -acetimidobenzoato	174.8	166.9	7.9
benzoato	175.1	167.4	7.7
<i>o</i> -benzoylbenzoato	173.8	167.0	6.8
<i>p</i> -benzoylbenzoato	174.0	166.6	7.4
<i>p</i> -formylbenzoato	173.9	166.6	7.3
<i>p</i> -formylcinnamato	175.3	167.1	8.2
maleato	175.6		
sorbato	176.0	167.6	8.4
acetato ^b	179.3	172.1	7.2

^a Chemical shift for the free acid in the same solution.

^b Corresponding rhodium(III) complex.

for which difficulties, such as contamination by the parent acid, with the anation methods has been reported in the literature.

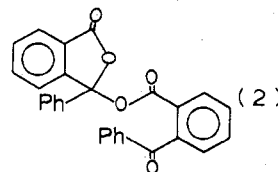
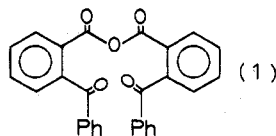
Gould and his co-workers have claimed that the preparation of carboxylato complexes from acid anhydrides is only successful for low molecular weight acids. Unfortunately, no experimental details of their attempts were reported and one cannot therefore define the reasons for their failure. In any event, three (*o*- and *p*-benzoylbenzoato and *p*-formylbenzoato complexes) of four cases which they categorically state cannot be prepared by the anhydride method gave, in our hands, excellent yields of analytically pure products. The experiments are explicitly described in the Experimental Section. Furthermore, either ¹³C (Table II) or proton spectroscopy demonstrated the absence of contamination by the parent acid, a problem which in a number of cases appears to have plagued Gould's preparations.^{4a-c,h,i} Failure in the case of the fourth ligand (*o*-formylbenzoato) is readily understood since the parent acid exists as the chain tautomer and does not yield an anhydride.²⁹ Thus the experimental evidence to date indicates that, provided the acid anhydride can be prepared, the method we have described is an excellent one for preparing (carboxylato)pentaamminecobalt(III) complexes.

Since comparatively few anhydrides are commercially available, it is usually convenient to prepare them in situ by reacting the acid with dicyclohexylcarbodiimide in DMF. The urea produced in this reaction is highly insoluble in water and does not complicate the purification of the complexes. It is, however, essential to add the aqua or hydroxo complex after the formation of the anhydride since otherwise some (*N,N*-dimethylformamido)pentaamminecobalt(III) salt is formed.³⁰

Maleic anhydride reacts as expected to yield the hydrogen maleato complex. An example of a binuclear complex is the preparation of decaammine-(μ -fumarato)-dicobalt(III). This is a case where the preparation of the acid anhydride is not feasible but acylation is readily effected through the bis(*p*-nitrophenyl) ester of fumaric acid. *p*-Nitrophenyl esters also offer the advantage that they may be used stoichiometrically

and thus eliminate all possible contamination by the carboxylate ion.

We noted above that *o*-formylbenzoic acid does not yield a normal anhydride. The literature suggests that the same is true of *o*-benzoylbenzoic acid.³¹ We have found that the normal anhydride **1** can be prepared from the acid by reaction



with dicyclohexylcarbodiimide. It is characterized by its ¹³C spectrum which exhibits only 12 absorptions in contrast to the much more complex spectrum of the pseudoanhydride **2**.³²

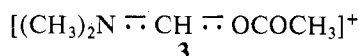
cis- and *trans*-Bis(acetato)bis(ethylenediamine)cobalt(III). All plausible mechanisms for the conversion of the hydroxo to the carboxylato ligand involved preservation of the cobalt-oxygen bond.³³ Thus, unlike anation, the reaction should proceed with retention of the stereochemistry of the central cobalt atom. We have now shown that the reactions of acetic anhydride with *cis*- and *trans*-diaquabis(ethylenediamine)cobalt(III) nitrates in the presence of *N,N*-dimethylbenzylamine proceed with complete retention of configuration to yield the corresponding bis(acetato)complexes. The stereochemical assignments are based on the equivalence and nonequivalence in the proton NMR of the methylene groups of the ethylenediamine ligand in the *trans* and *cis* isomers, respectively.

p-Nitrophenyl acetate, which, as stated above, readily acetylates hydroxopentaamminecobalt(III), failed to react with the *trans*-diaqua complex. Since the first dissociation constant for the diaqua complex in water is $pK_a = 4.5$ ³⁴ compared with $pK_a = 6.6$ ³⁴ for aquapentaamminecobalt(III), it is probable that the aquahydroxo anion is too weak a nucleophile to react with *p*-nitrophenyl acetate. The considerably more reactive 2,4-dinitrophenyl acetate, however, afforded the *trans*-bis(acetato)complex in theoretical yield.

(Acetato)pentaammine Complexes of Cr(III), Rh(III), and Ru(III). The acylation method can be extended to the preparation of (carboxylato)pentaamminechromium(III) salts. Thus Davies, Evans, and Jordan³⁵ have reported that the preparation of the trifluoroacetato complex by the anhydride procedure is superior to the anation reaction. We have, also prepared the analogous acetato complex by using 2,4-dinitrophenyl acetate as the acetylating agent.

(Acetato)pentaamminecobalt(III) trifluoromethanesulfonate was prepared in good yield from the aqua complex in DMF by treatment with acetic anhydride and *N,N*-dimethylbenzylamine. The analogous ruthenium(III) complex was obtained by the reaction of the hydroxo complex in aqueous ammonia with acetic anhydride.

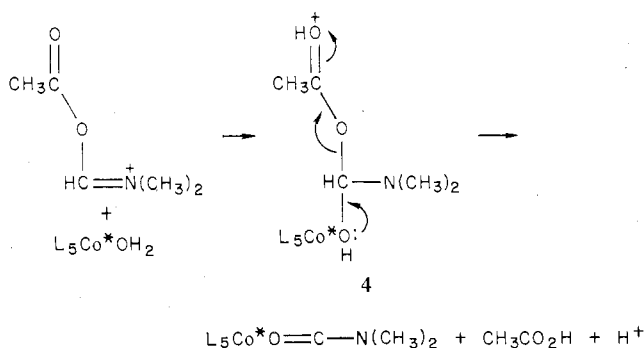
Attempted Acetylation of Aquapentaamminecobalt(III). We have attempted to effect a direct acetylation of the aqua rather than the hydroxo complex by a reaction with a powerful acetylating reagent, viz., $CH_3CO^+ClO_4^-$ -DMF in which the reacting species is presumably **3**. When 2 equiv of this reagent



was used, the only inorganic product isolated was (di-

Table III. Reactions of $\text{LCo}(\text{NH}_3)_5$ Salts with Acetyl Perchlorate in DMF at 25 °C

L	equiv of CH_3CO^+	mol % of product		
		L = OAc	L = DMF	L = OH_2
OH_2	0.5	0.5	28	71
	1.0	0.5	57	42
	1.5	0	75	25
	2.0	1	99	0
OH	0.5	5	61	34
	1.0	7	71	22
OAc	0.74	61	39	...
	2.0	1	99	0

Scheme I

methylformamido)pentaamminecobalt(III) perchlorate (Table III). The possibility that the DMF complex arises through the intermediacy of the (acetato)pentaammine was examined. It was shown that, under the same conditions, the acetato ligand is indeed replaced by DMF. Another experiment in which the aqua and acetato complexes were allowed to compete for an insufficiency of the reagents 3 revealed, that the pathway involving the acetato ligand is much slower.

The reaction with ^{18}O -labeled aqua complex yielded the DMF derivative with $92 \pm 3\%$ retention of the label. This result can be interpreted (Scheme I) in terms of an intermediate complex 4 which decomposes, by loss of acetic acid, to the DMF complex with essentially total retention of the label.³⁸

Registry No. (Acetato)pentaamminecobalt(III) perchlorate, 14523-28-5; (acetato)pentaamminecobalt(III) trifluoromethanesulfonate, 22239-79-8; (*p*-benzoylbenzoato)pentaamminecobalt(III) perchlorate, 69897-86-5; (*p*-formylbenzoato)pentaamminecobalt(III) perchlorate, 15523-31-6; (*o*-benzoylbenzoato)pentaamminecobalt(III) perchlorate, 69897-88-7; decaammine-(μ -fumarato)-dicobalt(III) perchlorate, 69897-90-1; *cis*-bis(acetato)bis(ethylenediamine)cobalt(III) acetate, 69897-91-2; *trans*-bis(acetato)bis(ethylenediamine)cobalt(III) nitrate, 69927-34-0; (acetato)pentaamminechromium(III) perchlorate, 22792-96-7; (acetato)pentaammine-rhodium(III) trifluoromethanesulfonate, 69897-92-3; (acetato)pentaammineruthenium(III) trifluoromethanesulfonate, 69897-93-4; (*N,N*-dimethylformamido)pentaamminecobalt(III) perchlorate, 69897-24-1; (benzoato)pentaamminecobalt(III) perchlorate, 30185-41-2; (*p*-acetamidobenzoato)pentaamminecobalt(III) perchlorate, 69897-95-6; (*p*-formylcinnamato)pentaamminecobalt(III) perchlorate, 69897-96-7; (hydrogen maleato)pentaamminecobalt(III) perchlorate, 30147-39-8; (isonicotinato)pentaamminecobalt(III) perchlorate, 69897-97-8; (pivalato)pentaamminecobalt(III) perchlorate, 14879-41-5; (sorbato)pentaamminecobalt(III) perchlorate, 69926-72-3; hydroxopentaamminecobalt(III) perchlorate, 18885-27-3; aquapentaamminecobalt(III) trifluoromethanesulfonate, 69897-22-9; aquapentaamminecobalt(III) perchlorate, 13820-81-0; *cis*-diaqua-bis(ethylenediamine)cobalt(III) nitrate, 16300-52-0; *cis*-dichloro-bis(ethylenediamine)cobalt(III) chloride, 14040-32-5; *trans*-diaqua-bis(ethylenediamine)cobalt(III) nitrate, 17967-05-4; *trans*-dichlorobis(ethylenediamine)cobalt(III) chloride, 14040-33-6; aquapentaamminechromium(III) perchlorate, 32700-25-7; aquapenta-

amminechromium(III) nitrate, 19683-62-6; aquapentaammine-rhodium(III) trifluoromethanesulfonate, 69897-98-9; chloropenta-ammineruthenium(III) dichloride, 18532-87-1; *p*-nitrophenyl acetate, 830-03-5; *o*-benzoylbenzoic acid, 85-52-9; sodium 2,4-dinitrophenylate, 6226-55-7; fumaryl chloride, 25144-43-8; bis(2,4-dinitrophenyl) fumarate, 69897-41-2; *o*-benzoylbenzoic anhydride, 59022-17-2; 2,4-dinitrophenyl acetate, 4232-27-3; acetic anhydride, 108-24-7; acetyl perchlorate, 2889-74-9; *p*-benzoylbenzoic anhydride, 6158-55-0; *p*-formylbenzoic anhydride, 69897-42-3.

References and Notes

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