accelerated in polar solvents for Ia and Ib, and this solvent effect may well prove to be a useful criterion for identifying preliminary ionization effects in organometallic reaction mechanisms.

Experimental Section

[PtClMe(bpy)] was prepared by the literature method.[2]

[PtClMe(MeO$_2$CC≡CCO$_2$Me)(bpy)]. MeO$_2$CC≡CCO$_2$Me (0.15 mL) was added to [PtClMe(bpy)] (0.18 g) in dry acetone (50 mL), and the mixture was stirred for 1 h. The white precipitate was filtered off, washed thoroughly with ether, and dried under vacuum. The yield was 0.13 g. Anal. Calcd for $C_{17}H_{17}ClN_2O_4Pt$: C, 37.5; H, 3.1; Pt, 35.9. Found: C, 37.1; H, 3.0; Pt, 35.7.

[PtClMe(CF$_3$C≡CCF$_3$)(bpy)]. Hexafluorobut-2-yne (5 mmol) was condensed into a Carius tube containing [PtClMe(bpy)] (0.19 g) in acetone (10 mL), the solution was cooled by liquid nitrogen, and the tube was then sealed and allowed to warm to room temperature. The tube was shaken at room temperature for 12 h and then opened, and the white precipitate was filtered off, washed with ether, and recrystallized from CH$_2$Cl$_2$. The yield was 0.19 g. Anal. Calcd for $C_{15}H_{11}F_6ClN_2Pt$: C, 25.6; H, 2.2; N, 5.4; F, 22.1. Found: C, 25.4; H, 2.0; N, 5.3; F, 20.9.

PtIMe(CF$_3$C≡CCF$_3$)(bpy)] was prepared similarly from [PtIMe(bpy)]. The yield was 71%. Anal. Calcd for $C_{15}H_{11}F_6IN_2Pt$: C, 21.8; H, 1.8; F, 18.8. Found: C, 21.4; H, 1.6; F, 18.4.

Kinetic Studies. Changes in UV–visible spectra were recorded as reaction proceeded with solutions of the alkyne complexes (10^{-4} M) in 1-cm quartz cuvettes held in the thermostated electrically heated cell compartment of a Unicam SP 8000 spectrophotometer. Solutions were made up immediately prior to the kinetic run.

Registry No. Ia, 75764-67-9; Ib, 75764-68-0; Ic, 75764-69-1; Id, 75764-70-4; PtClMe(bpy), 50726-77-7; PtIMe(bpy), 71674-45-8.

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Labile (Trifluoromethanesulfonato)cobalt(III) Amine Complexes

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Facile synthetic routes to cobalt(III) amine complexes of the labile unidentate trifluoromethanesulfonate anion ($CF_3SO_3^-$), namely, $Co(NH_3)_5(OSO_2CF_3)^{2+}$, *cis*-$Co(en)_2(OSO_2CF_3)_2{}^+$, and *fac*-$Co(dien)(OSO_2CF_3)_3$, are reported. The use of these complexes as synthetic precursors for a range of complexes involving direct solvolysis or reactions in poorly coordinating solvents such as sulfolane or acetone is described. For example, in the pentaamminecobalt(III) system, syntheses of $Co(NH_3)_5L^{n+}$ (L = OH_2, NH_3, $OHCH_3$, $OHCH_2CH_3$, $OHCH(CH_3)_2$, $NCCH_3$, $OP(OCH_3)_3$, $OCH{\cdot}N(CH_3)_2$, $OS(CH_3)_2$, $OC(NH_2)_2$, $NCNH_2$, $^-OOCCH_3$, $^-OOCCHCl_2$) in high yield are reported. The kinetics and the stereochemical course of aquation of the labile trifluoromethanesulfonato complexes and derivatives are reported.

Introduction

The trifluoromethanesulfonyl group (CF_3SO_2), by virtue of the large inductive effect of the trifluoromethyl group, is one of the strongest electron-withdrawing groups known.[2–4] Consequently, the trifluoromethanesulfonate anion ($CF_3SO_3^-$, triflate) has found use as an excellent leaving group in nucleophilic substitution reactions in organic chemistry.[4,5] The triflate anion may act as a unidentate ligand in inorganic coordination chemistry. Recently, characterizations of the labile pentaamminecobalt(III) complexes of both trifluoromethanesulfonate ($OSO_2CF_3^-$) and perchlorate ($OClO_3^-$) have been reported.[6,7] The perchlorato and triflato ligands aquate with rate constants of 0.1 and 0.027 s^{-1}, respectively (25 °C, μ = 1.0 M). The lability of these coordinated anions raises the prospect of their complexes providing facile routes to a range of cobalt(III) complexes via substitution reactions. However, since complexes containing the more labile perchlorate ligand are potentially explosive, we have chosen to concentrate attention on the triflato complexes.

Prior to this study, synthesis of $Co(NH_3)_5OSO_2CF_3{}^{2+}$ has involved nitrosation of azidopentaamminecobalt(III) in triflate medium and rapid isolation of the product.[7,8] We have now developed a simple procedure which yields the triflate complex quantitatively from chloropentaamminecobalt(III) and have extended this preparative concept to other cobalt(III) amine systems.

Dissolution of the triflato complexes in a range of solvents provides facile routes to complexes containing the coordinated solvents, while reaction with ligands in poorly coordinating solvents such as sulfolane (1,1-dioxothiolane) or acetone proceeds smoothly with substitution of the coordinated triflate by the ligand. Examples of the use of these procedures in some otherwise difficult syntheses are presented.

Experimental Section

Visible absorption spectra were recorded in duplicate by using Cary 14 or Cary 118 recording spectrophotometers. ^{1}H NMR spectra were measured with JEOL Minimar (100 MHz) or JEOL AMX60 spectrometers at ~30 °C, with use of sodium trimethylsilylpropionate as internal reference. Infrared spectra (KBr disk) were recorded with a Perkin-Elmer Model 457 instrument.

Anhydrous trifluoromethanesulfonic acid (CF_3SO_3H, 3M Company) was vacuum distilled (bp 52 °C at 10 mmHg). The precursor complexes $[Co(NH_3)_5Cl]Cl_2$,[9] *cis*-$[Co(en)_2Cl_2]Cl$,[10] *trans*-$[Co(en)_2Cl_2]Cl$,[10] *cis*-$[Co(en)_2CO_3]Cl$,[11] and $Co(dien)Cl_3$[12] were synthesized by reported methods.[13] Analytical reagent grade or redistilled

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solvents were used. Sulfolane was vacuum distilled after drying by passage through a column of molecular sieves.

1. (Trifluoromethanesulfonato)cobalt(III) Amine Complexes. $[Co(NH_3)_5OSO_2CF_3](CF_3SO_3)_2$. To $[Co(NH_3)_5Cl]Cl_2$ (50 g) in a three-necked round-bottom flask (2 L) fitted with a gas bubbler was cautiously added anhydrous CF_3SO_3H (0.3 L). A steady stream of argon or nitrogen was passed through the resulting solution as it was warmed to and maintained at 90–100 °C. After the evolution of HCl had ceased (~1 h, monitored by passing the effluent gas through a solution of $AgNO_3$), the flask was cooled in an ice bath to 0 °C. The gas flow was discontinued, and diethyl ether (0.5 L) was added dropwise with vigorous mechanical stirring. After further dilution with ether to ~1.6 L, the violet suspension was transferred to screw-capped plastic bottles and centrifuged. The supernatant was retained to recover the excess triflate as the sodium salt. The pellets were resuspended in ether (~1 L) and recentrifuged (three times), then resuspended in a small volume of ether, and filtered under vacuum through a large sintered glass funnel (porosity grade 4). After repeated washing with ether, the isolated solid was ground in a mortar and thoroughly dried in vacuo over P_2O_5. The violet powder (116 g, 98% yield) is best stored in a desiccator but is stable for at least 3 months sealed from the atmosphere. Anal. Calcd for $C_3H_{15}N_5F_9O_9S_3Co$: C, 6.09; H, 2.56; N, 11.84; F, 28.92; S, 16.27; Co, 9.96. Found: C, 6.3; H, 3.0; N, 11.6; F, 28.5; S, 16.4; Co, 9.7. The product analyzed for very small amounts of $(CH_3CH_2)_2OH^+{\cdot}CF_3SO_3^-$ in all preparations but was adequate for preparative purposes. A small quantity was recrystallized in low yield by filtering a freshly prepared ice-cold aqueous solution directly into a stirred concentrated aqueous solution of $NaCF_3SO_3$ at −10 °C. The violet crystals were immediately collected, washed with a little ethanol and then ether, and dried in vacuo over P_2O_5. Anal. Found: C, 6.1; H, 2.4; N, 11.7; S, 16.1.

***cis*-$[Co(en)_2(OSO_2CF_3)_2](CF_3SO_3)$.** The bis(ethylenediamine)cobalt(III) complex was prepared from either $[Co(en)_2Cl_2]Cl$ (A) or $[Co(en)_2CO_3]Cl$ (B).

Method A. Nitrogen was bubbled through a solution of *cis*-$[Co(en)_2Cl_2]Cl$ (13.6 g) in anhydrous CF_3SO_3H (60 mL), as it was heated at 90–100 °C for 3 h, essentially as described above for the pentaammine complex. After the solution was cooled, diethyl ether (0.25 L) was added slowly with vigorous stirring. The solid was filtered, triturated on the frit with ether (~100 mL), and dried in air. The product was ground in a mortar, boiled in chloroform (~100 mL) for 10 min to remove traces of CF_3SO_3H, filtered, washed with ether, and dried in vacuo over P_2O_5, to give a free-flowing purple powder (27 g, 94% yield). Anal. Calcd for $C_7H_{16}N_4F_9O_9S_3Co$: C, 13.42; H, 2.57; N, 8.95; F, 27.30; S, 15.36. Found: C, 13.1; H, 2.6; N, 8.5; F, 26.8; S, 15.2. Alternatively, *trans*-$[Co(en)_2Cl_2]Cl$ was used as the starting material. The product is identical with that described above and is apparently the cis isomer.

Method B. Solid $[Co(en)_2CO_3]Cl$ (8 g) was slowly added to stirred anhydrous CF_3SO_3H (25 mL) at room temperature. Dry nitrogen was then bubbled through the purple solution for 15 min in order to ensure complete removal of CO_2 and HCl evolved during the reaction. The solution was stirred in an ice bath as ether (125 mL) was added dropwise. The purple product (15.6 g, 95% yield) was isolated as described above (method A). Anal. Found: C, 13.4; H, 3.1; N, 8.5; F, 26.9.

The product was recrystallized as the perchlorate salt by dissolution of the triflate salt in a minimum of cold (~10 °C) water which was filtered immediately into iced 70% $HClO_4$. After the ice had melted, the precipitate was collected, washed with ethanol and ether, and dried in vacuo over P_2O_5. Anal. Calcd for $C_6H_{16}N_4F_6O_{10}S_2ClCo$: C, 12.49; H, 2.80; N, 9.72; F, 19.76; S, 11.12; Cl, 6.15. Found: C, 12.6; H, 3.2; N, 9.5; F, 19.6; S, 11.4; Cl, 6.3.

$Co(dien)(OSO_2CF_3)_3$. $Co(dien)Cl_3$ (12.8 g) and anhydrous CF_3SO_3H (50 mL) were heated under nitrogen for 3 h at 100–110 °C, essentially as described above for the preparation of $Co(en)_2(OSO_2CF_3)_2^+$ (method A). The bright purple product was precipitated by slow addition of ether (0.2 L) to the cooled, stirred solution, then collected, purified by boiling in chloroform as described above, and dried in vacuo over P_2O_5 (26 g, 90% yield). Anal. Calcd for $C_7H_{13}N_3F_9O_9S_3Co$: C, 13.80; H, 2.15; N, 6.90; F, 28.06; S, 15.78. Found: C, 13.9; H, 2.5; N, 6.5; F, 27.4; S, 15.8.

2. Pentaamminecobalt(III) Derivatives. Pentaamminecobalt(III) complexes containing coordinated solvents were generally prepared simply by solvolysis of (triflato)pentaamminecobalt(III) triflate in the appropriate pure solvent. Other complexes were prepared by reaction with a solution of the ligand in the poorly coordinating solvents, sulfolane or acetone.

$[Co(NH_3)_5OH_2](ClO_4)_3$. $[Co(NH_3)_5OSO_2CF_3](CF_3SO_3)_2$ (3 g) was dissolved in water (30 mL, ~25 °C) to give an orange-red solution, which was warmed to 60 °C. Addition of 70% $HClO_4$ to the first sign of cloudiness followed by slow cooling afforded large crystals of the perchlorate salt of the product, which were collected by filtration, washed with ethanol and ether and dried in air (2.2 g, 94% yield). Anal. Calcd for $H_{17}N_5O_{13}ClCo$: H, 3.72; N, 15.21; Cl, 23.10; Co, 12.80. Found: H, 3.6; N, 15.2; Cl, 23.3; Co, 12.4. This method also provides a simple route to ^{17}O- or ^{18}O-labeled $Co(NH_3)_5OH_2^{3+}$ since aquation proceeds exclusively with cobalt–oxygen cleavage.[7] Dissolution in labeled water was followed by freeze-drying, with recovery of the distilled solvent. Prolonged vacuum-drying of the lyophilized solid produced a pure dry sample of $^{17}OH_2$-labeled $[Co(NH_3)_5OH_2](CF_3SO_3)_3$. Anal. Calcd for $C_3H_{17}N_5F_9{}^{17}OO_9S_3Co$: C, 5.91; H, 2.81; N, 11.49; S, 15.78. Found: C, 6.0; H, 2.8; N, 11.3; S, 15.4.

$[Co(NH_3)_6](ClO_4)_3$. $[Co(NH_3)_5OSO_2CF_3](CF_3SO_3)_2$ (3 g) was dissolved in liquid ammonia (~0.2 L), giving immediately an orange solution. The yellow solid obtained on removal of the solvent at reduced pressure was recrystallized from warm (50 °C) ~1 M $HClO_4$ on slow cooling (2.1 g, 89% yield). Anal. Calcd for $H_{18}N_6O_{12}Cl_3Co$: H, 3.95; N, 18.29; Cl, 23.15; Co, 12.83. Found: H, 3.8; N, 18.5; Cl, 23.0; Co, 12.8.

$[Co(NH_3)_5OHCH_2CH_3](CF_3SO_3)_3$. $[Co(NH_3)_5OSO_2CF_3](CF_3SO_3)_2$ (3 g) was dissolved in refluxing absolute ethanol (0.2 L, <10 min). On cooling to −10 °C, the red solution deposited flakes, which were collected by filtration, washed with ether, and dried in vacuo over P_2O_5 (2.05 g, 63% yield). Anal. Calcd for $C_5H_{21}N_5F_9O_{10}S_3Co$: C, 9.42; H, 3.32; N, 10.99; F, 26.83; S, 15.09; Co, 9.25. Found: C, 9.3; H, 3.5; N, 10.8; F, 25.9; S, 14.8; Co, 9.3. Visible spectrum (λ_{max}, nm, (ϵ_{max}, M^{-1} cm^{-1})) in ethanol: 506 (50.4), 346 (51.3). ^1H NMR: δ 2.78 (3 H, br, trans NH_3), 3.98 (12 H, br, cis NH_3), 1.11 (3 H, t, CH_3), 3.24 (2 H, quar, CH_2) in Me_2SO-d_6. The complex solvolyzed to $Co(NH_3)_5OS(CD_3)_2^{3+}$ and free ethanol with $t_{1/2} \approx 30$ min at ~30 °C (observed by ^1H NMR, with spin decoupling). Alternatively, essentially pure product may be obtained in quantitative yield simply by evaporating the reaction mixture to dryness at reduced pressure at room temperature.

$[Co(NH_3)_5OHCH_3](CF_3SO_3)_3$. $[Co(NH_3)_5OSO_2CF_3](CF_3SO_3)_2$ (3 g) was dissolved in absolute methanol (25 mL) with gently warming (3 min). The pink crystals which deposited from the red solution on addition of diethyl ether (30 mL) and cooling were collected, washed with ether, and dried in vacuo over P_2O_5 (2.6 g, 81% yield). Anal. Calcd for $C_4H_{19}N_5F_9O_{10}S_3Co$: C, 7.71; H, 3.07; N, 11.24; F, 27.43; S, 15.43; Co, 9.45. Found: C, 8.0; H, 3.4; N, 11.2; F, 27.0; S, 15.5; Co, 9.1. Visible spectrum (λ_{max}, nm (ϵ_{max})) in methanol: 503 (46.6), 347 (46.4). ^1H NMR: δ 2.80 (3 H, trans NH_3), 3.98 (12 H, cis NH_3), 2.90 (3 H, CH_3) in Me_2SO-d_6. Over a period of hours in the NMR tube at room temperature the complex solvolyzed to $Co(NH_3)_5OS(CD_3)_2^{3+}$ [δ 2.67 (3 H, trans NH_3), 3.91 (12 H, cis NH_3)] and free methanol [δ 3.22 (3 H, CH_3)].

$[Co(NH_3)_5OHCH(CH_3)_2](CF_3SO_3)_3$. $[Co(NH_3)_5OSO_2CF_3](CF_3SO_3)_2$ (2 g) was dissolved in dry acetone (50 mL), and isopropyl alcohol (100 mL) was added. The solvent was removed at reduced pressure until the product began to crystallize. On cooling, the mixture deposited fine pink crystals which were collected by filtration, washed with isopropyl alcohol and ether, and dried in vacuo over P_2O_5 (1.6 g, 73% yield). The complex was best stored at 4 °C, since it slowly decomposed at room temperature with loss of isopropyl alcohol. Anal. Calcd for $C_6H_{23}N_5F_9O_{10}S_3Co$: C, 11.06; H, 3.56; N, 10.75; F, 26.25; S, 14.77; Co, 9.05. Found: C, 11.1; H, 3.5; N, 10.8; F, 26.0; S, 14.5; Co, 9.0. ^1H NMR: δ 2.52 (3 H, trans NH_3), 3.82 (12 H, cis NH_3), 1.21 (6 H, d, CH_3) in Me_2SO-d_6; δ 4.2 (15 H, br, NH_3), 1.21 (6 H, d, CH_3), 3.26 (1 H, m, CH) in D_2O. Over ~1 h in D_2O at 30 °C, the complex aquated to $Co(NH_3)_5OD_2^{3+}$ and free isopropyl alcohol [δ 1.14 (6 H, d, CH_3)].

$[Co(NH_3)_5NCCH_3](ClO_4)_2(CF_3SO_3)$. A suspension of $[Co(NH_3)_5OSO_2CF_3](CF_3SO_3)_2$ (3 g) in acetonitrile (20 mL) was stirred for 4 h at room temperature. The yellow product was collected by filtration, washed with ether, and dried in air. It was recrystallized as a mixed salt from ~0.1 M $NaCF_3SO_3$ by slow addition of saturated

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(13) Satisfactory microanalyses and spectroscopic data consistent with the literature were obtained in each case.

aqueous $NaClO_4$ at room temperature, collected, washed thoroughly with ethanol and ether, and dried in air (2.2 g, 81% yield). Anal. Calcd for $C_3H_{18}N_6F_3O_{11}SCl_2Co$: C, 6.76; H, 3.40; N, 15.76; S, 6.01; Co, 11.05. Found: C, 6.7; H, 3.5; N, 16.0; S, 5.9; Co, 10.9. ^1H NMR: δ 2.56 (3 H, s, CH_3), 3.32 (3 H, trans NH_3), 3.75 (12 H, cis NH_3) in Me_2SO-d_6.

$[Co(NH_3)_5OP(OCH_3)_3](ClO_4)_3\cdot H_2O$. A solution of $[Co(NH_3)_5OSO_2CF_3](CF_3SO_3)_2$ (3 g) in trimethyl phosphate (25 mL) was stirred at room temperature for 4 h and then added dropwise to vigorously stirred diethyl ether (0.5 L). The pink solid was collected, washed thoroughly with ether, then dissolved in cold water (30 mL), and filtered. The addition of solid $NaClO_4$ to the filtrate produced crystals which were filtered, washed with ethanol and ether, and dried in air (1.8 g, 59% yield). Anal. Calcd for $C_3H_{26}N_5O_{17}PCl_3Co$: C, 6.00 H, 4.36; N, 11.66; P, 5.16; Cl, 17.71; Co, 9.81. Found: C, 6.1; H, 4.3; N, 11.5; P, 5.0; Cl, 17.9; Co, 9.7. ^1H NMR (100 MHz): δ 2.61 (3 H, trans NH_3), 4.05 (12 H, cis NH_3), 3.53 (2 H, H_2O), 3.70, 3.81 (9 H, ^{31}P-coupled CH_3 doublet) in Me_2SO-d_6. The complex solvated with $t_{1/2} < 15$ min to give $Co(NH_3)_5OS(CD_3)_2{}^{3+}$ [δ 2.64 (3 H, trans NH_3), 3.87 (12 H, cis NH_3)] and free trimethyl phosphate (^{31}P-coupled doublet at δ 3.63, 3.74). The triflate salt was crystallized in lower yield (0.9 g, 24%) from the aqueous solution of the crude product by addition of solid $NaCF_3SO_3$. It was collected, washed thoroughly with ether, and dried in vacuo over P_2O_5. Anal. Calcd for $C_6H_{24}N_5F_9O_{13}PS_3Co$: C, 9.85; H, 3.31; N, 9.58; F, 23.38; P, 4.24; S, 13.15; Co, 8.06. Found: C, 9.8; H, 3.2; N, 9.6; F, 23.7; P, 4.4; S, 13.4; Co, 7.8.

$[Co(NH_3)_5OCH\cdot N(CH_3)_2](CF_3SO_3)_3\cdot H_2O$. A solution of $[Co(NH_3)_5OSO_2CF_3](CF_3SO_3)_2$ (3 g) in dimethylformamide (15 mL) was stirred for 15 min at room temperature and then added dropwise to vigorously stirred ether (1 L). The pink solid was collected, washed with ether, then redissolved in water (50 mL), and filtered. Slow addition of a concentrated aqueous solution of $NaCF_3SO_3$ to the filtrate (cooled to 0 °C) afforded red crystals, which were collected and washed with ether and then dried in vacuo over P_2O_5 (2.8 g, 81% yield). Anal. Calcd for $C_6H_{24}N_6F_9O_{11}S_3Co$: C, 10.56; H, 3.55; N, 12.32; F, 25.06; S, 14.10; Co, 8.64. Found: C, 10.6; H, 3.3; N, 12.3; F, 24.9; S, 14.2; Co, 8.5. ^1H NMR (100 MHz): δ 2.79 (3 H, trans NH_3), 3.90 (12 H, cis NH_3), 2.91 (3 H, CH_3), 3.08 (3 H, CH_3), 7.47 (1 H, CHO) in Me_2SO-d_6.

$[Co(NH_3)_5OS(CH_3)_2](CF_3SO_3)_3$. A solution of $[Co(NH_3)_5OSO_2CF_3](CF_3SO_3)_2$ (3 g) in dimethyl sulfoxide (10 mL) was stirred for 40 min at room temperature and then washed into a conical flask (1 L) with ethanol (20 mL). Ether (0.6 L) was slowly added with vigorous stirring. Upon standing, an oily red Me_2SO phase settled. The ether phase was decanted off through a sintered glass funnel (porosity 4). The oily residue was redissolved in ethanol (20 mL), and the complex reprecipitated by addition of ether (0.6 L). The precipitate was filtered on the same funnel, washed with ether, and air dried. This product was dissolved in water (30 mL) and deposited deep red-violet crystals on cooling and after the addition of concentrated aqueous $NaCF_3SO_3$. These were collected, washed with a little 50% (v/v) ethanol–ether, and dried in vacuo over P_2O_5 (2.8 g, 82% yield). Anal. Calcd for $C_5H_{21}N_5F_9O_{10}S_4Co$: C, 8.97; H, 3.16; N, 10.46; F, 25.54; S, 19.16; Co, 8.80. Found: C, 9.1; H, 3.2; N, 10.5; F, 25.4; S, 19.0; Co, 8.5. ^1H NMR: δ 2.68 (3 H, trans NH_3), 3.91 (12 H, cis NH_3), 2.77 (6 H, CH_3) in Me_2SO-d_6.

$[Co(NH_3)_5OC(NH_2)_2](S_2O_6)_{3/2}\cdot 1^1/_2H_2O$. To a stirred solution of recrystallized urea (12 g) in sulfolane (200 mL) was slowly added $[Co(NH_3)_5OSO_2CF_3](CF_3SO_3)_2$ (20 g). The solution was stirred for 75 min at room temperature and then washed into a large flask with ethanol (30 mL). Ether (1.5 L) was added with vigorous stirring, and the phases were allowed to separate. The ether phase was decanted through a bed of Hyflo Supercel filter aid on a sintered glass funnel. The viscous oily red residue was repeatedly treated (five times) with ethanol (30 mL) and then ether (1.5 L) in a similar manner until a solid residue remained on the walls of the flask and on the filter bed. The compound in the flask was dissolved in a minimum of water and transferred to the filter bed, and the filtrate was collected (~80 mL, with washings). Pink crystals of essentially pure $[Co(NH_3)_5OC(NH_2)_2](ClO_4)_3$ which deposited on treatment of the filtrate with solid $NaClO_4$ (almost to saturation) were collected by filtration, washed with ethanol and ether, and dried in air (15.6 g, 92% yield). The ^1H NMR spectrum in Me_2SO-d_6, and the infrared spectrum ($\nu_{C=O}$ = 1640 cm^{-1}) confirmed that the product contained only the O-bound isomer.[14] No cyanate complex was observed in the infrared spectrum. This product was crystallized as the dithionate salt by treatment of a concentrated aqueous solution (~0.3 L) at room temperature with $Na_2S_2O_6\cdot 2H_2O$ (15.6 g) while being stirred over 10 min, collected by filtration, washed with 50% aqueous ethanol, ethanol, and ether, and dried in vacuo over P_2O_5. Anal. Calcd for $C_2H_{44}N_{14}O_{23}S_6Co_2$: C, 2.55; H, 4.70; N, 20.80; S, 20.41; Co, 12.50. Found: C, 2.4; H, 4.7; N, 21.0; S, 20.3; Co, 12.6.

$[Co(NH_3)_5NCNH_2](ClO_4)_3\cdot {}^1/_2H_2O$. Cyanamide (5 g, Ega Chemie, 96–98%) was dissolved with stirring in sulfolane (100 mL) at room temperature. $[Co(NH_3)_5OSO_2CF_3](CF_3SO_3)_2$ (5 g) was added, and stirring continued for a further 17 h. The orange solution was diluted into 2 L of 10^{-3} M $HClO_4$ and sorbed onto a column (5 × 19 cm) of SP-Sephadex C25 (Na^+ form), which was then washed with water and eluted with 0.3 M $NaClO_4$. The eluant containing the major orange band was concentrated on a rotary evaporator, yielding orange flakes which were collected, washed with ethanol and ether, and dried in air (3.2 g, 77% yield). Anal. Calcd for $C_2H_{36}N_{14}O_{25}Cl_6Co_2$: C, 2.43; H, 3.68; N, 19.87; Cl, 21.55; Co, 11.94. Found: C, 2.4; H, 3.6; N, 20.0; Cl, 21.5; Co, 11.7. ^1H NMR: δ 3.23 (3 H, trans NH_3), 3.70 (12 H, cis NH_3), 8.09 (2 H, NH_2) in Me_2SO-d_6.

$[Co(NH_3)_5(OOCCH_3)](ClO_4)_2\cdot 1^1/_2H_2O$. $[Co(NH_3)_5OSO_2CF_3](CF_3SO_3)_2$ (1 g) was suspended in glacial acetic acid (30 mL) and anhydrous sodium acetate (~0.1 g) added. The suspension was stirred at room temperature for 15 min, when all the solid complex had dissolved. The solvent was removed at reduced pressure. The red product was dissolved in water (20 mL), and solid $LiClO_4$ was added until crystallization commenced. After the solution was cooled to 0 °C, the solid was collected by filtration, washed with methanol and ether, and dried in air (0.65 g, 90% yield). Anal. Calcd for $C_4H_{40}N_{10}O_{23}Cl_4Co_2$: C, 5.93; H, 5.22; N, 17.29; Cl, 17.50; Co, 14.55. Found: C, 6.1; H, 4.5; N, 17.3; Cl, 17.5; Co, 14.4. ^1H NMR: δ 2.69 (3 H, trans NH_3), 3.72 (12 H, cis NH_3), 1.84 (3 H, s, CH_3), 3.40 (3 H, s, H_2O) in Me_2SO-d_6.

$[Co(NH_3)_5(OOCCHCl_2)](ClO_4)_2\cdot 1^1/_2H_2O$. $[Co(NH_3)_5OSO_2CF_3](CF_3SO_3)_2$ (1 g) was suspended in distilled dry dichloroacetic acid, and dry distilled triethylamine (~0.1 mL) was added as base. The suspension was stirred and warmed (~40 °C) until complete dissolution of the complex had occurred. After the solution was cooled to room temperature, an equal volume of ice-cold water was added, followed immediately by excess solid $LiClO_4$. Stirring for 1 min in an ice bath led to precipitation of a pink microcrystalline solid, which was immediately collected, washed with a little ice-cold water, and then thoroughly washed with methanol to remove any undissolved $LiClO_4$. It was dried in air after further washing with ether (0.55 g, 70% yield). Anal. Calcd for $C_4H_{38}N_{10}O_{23}Cl_8Co_2$: C, 5.07; H, 4.04; N, 14.78; Cl, 29.92; Co, 12.43. Found: C, 5.2; H, 3.5; N, 15.0; Cl, 30.1; Co, 12.0. ^1H NMR: δ 2.71 (3 H, trans NH_3), 3.80 (12 H, cis NH_3), 2.58 (1 H, s, $CHCl_2$), 3.41 (3 H, s, OH_2) in Me_2SO-d_6.

Sodium Trifluoromethanesulfonate, $NaO_3SCF_3\cdot H_2O$. Large amounts of ethereal solutions of trifluoromethanesulfonic acid were recovered from the separation of the triflato complexes from their reaction mixtures. The expensive triflate can be readily recovered as the sodium salt. To the vigorously stirred ethereal solution was *cautiously* added an equal volume of water. A stream of compressed air was passed over the surface of the stirred solution in a fume cupboard to remove the bulk of the ether as concentrated NaOH solution (~10 M) was cautiously added. After the aqueous solution had been neutralized (pH ~6), the solvent was removed at reduced pressure. The white solid was recrystallized from a minimum of hot water (>80 °C) and dried in vacuo over P_2O_5. Alternatively, white flakes were obtained in better yield from boiling methanol, but the product contained both water and methanol of crystallization.

3. Bis(ethylenediamine)cobalt(III) Derivatives. ***cis*-$[Co(en)_2(HOCH_3)_2](CF_3SO_3)_3$.** *cis*-$[Co(en)_2(OSO_2CF_3)_2](CF_3SO_3)$ (1 g) was dissolved in AR dry methanol (100 mL) and stirred at room temperature in a closed flask for 2 days. The pink solution was concentrated on a rotary evaporator and ether added slowly with stirring to precipitate a pink solid in high yield. Following separation on a sintered funnel, the solid was redissolved in dry methanol and precipitated again by ether addition. The filtered pink solid was washed with ether, air-dried, and then dried in vacuo over P_2O_5 for 1 h (1.0 g, 90% yield). Anal. Calcd for $C_9H_{22}N_4F_9O_{11}S_3Co$: C, 15.70; H, 3.22; N, 8.14; S, 13.97. Found: C, 14.9; H, 3.4; N, 8.2; S, 14.3. ^1H

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(14) Balahura, R. J.; Jordan, R. B. *Inorg. Chem.* **1970**, *9*, 1567.

NMR: δ 6.50, 5.95 (8 H, br, NH_2), 3.18 (6 H, s, CH_3), 3.02, 2.64 (8 H, br, CH_2) in 0.01 M DCl. After 3 h of heating in a steam bath, a singlet corresponding to free methanol (δ 3.22) was observed. Visible absorption maxima (λ, nm (ϵ)): 496 (85.2), 361 (71.2) in methanol.

***cis*-[$Co(en)_2(Me_2SO)_2](ClO_4)_3$.** *cis*-[$Co(en)_2(OSO_2CF_3)_2](CF_3SO_3)$ (2 g) was dissolved in a minimum volume of dry dimethyl sulfoxide, and the solution was warmed (~50 °C) for $^1/_2$ h. Ether (~$^1/_2$ L) was added slowly to the stirring cooled solution to precipitate quantitatively the purple product. This compound was recrystallized from a minimum volume of water upon the addition of saturated $NaClO_4$ solution (1:5 v/v) and cooling and was collected, washed with ethanol and ether, and dried in vacuo (yield 1.4 g, 80%). Anal. Calcd for $C_8H_{28}N_4Cl_3S_2O_{14}Co$: C, 15.16; H, 4.45; N, 8.84; S, 10.12. Found: C, 15.1; H, 4.5; N, 8.6; S, 10.0. ^1H NMR: δ 6.2, 4.3 (8 H, br, NH_2), 2.68, 2.40 (8 H, br, CH_2), 2.63 (12 H, CH_3) in Me_2SO-d_6.

***cis*-[$Co(en)_2(NCCH_3)_2](NO_3)(ClO_4)_2 \cdot H_2O$.** *cis*-[$Co(en)_2(OSO_2CF_3)_2](CF_3SO_3)$ (2 g) was dissolved in a minimum volume of AR dry acetonitrile and stirred in a closed flask for 2 h. The crude product was isolated nearly quantitatively by addition of ether (~$^1/_2$ L). This yellow solid was dissolved in a minimum volume of warm water and crystallized by addition of excess saturated $LiClO_4/LiNO_3$ (1:1) mixture and cooling. The yellow crystals were collected, washed with ethanol and ether, and dried in vacuo over P_2O_5 (1.4 g, 80% yield). Anal. Calcd for $C_8H_{24}N_7Cl_2O_{12}Co$: C, 17.79; H, 4.48; N, 18.16; Cl, 13.13. Found: C, 18.1; H, 4.7; N, 18.1; Cl, 13.2.

Authentic samples of both *cis*- and *trans*-$Co(en)_2(NCCH_3)_2^{3+}$ were prepared by a separate method involving nitrosation of coordinated azide, as detailed below. *cis*-[$Co(en)_2(N_3)_2](ClO_4)$ (5 g) stirred in dry acetonitrile (250 mL) was treated with an approximately twofold molar excess of nitrosyl triflate.[7] Rapid reaction occurred as the diazido complex dissolved, yielding a yellow solution of the required complex. The product was precipitated quantitatively by slow addition of ether (~$1^1/_4$ L) to the stirred solution. This solid proved to be a mixture of cis and trans isomers in an approximate 7:3 ratio. Reaction in an exactly analogous manner of *trans*-[$Co(en)_2(N_3)_2](ClO_4)$ yielded a cis/trans mixture in an approximately 1:1 ratio.

To a stirred aqueous solution of the crude mixture was added excess saturated $NaClO_4$ solution (1:5 v/v). The trans isomer was precipitated selectively and was recrystallized twice from water as orange-yellow needles of the triperchlorate salt upon addition of saturated $NaClO_4$ solution. Anal. Calcd for $C_8H_{22}N_6Cl_3O_{12}Co$ (trans isomer): C, 17.17; H, 3.96; N, 15.02; Cl, 19.00. Found: C, 16.9; H, 4.0; N, 14.9; Cl, 19.2. ^1H NMR: δ 6.00 (8 H, s, NH_2), 2.80 (8 H, s, CH_2), 2.52 (6 H, s, CH_3) in Me_2SO-d_6. To the initial filtrate from the trans crystallization was added excess solid $LiNO_3$. The cis isomer (as the $(ClO_4)_2(NO_3) \cdot H_2O$ salt) crystallized upon cooling. This product was recrystallized twice from water by addition of saturated $LiClO_4/LiNO_3$ (1:1, 1:5 v/v) solution and isolated as yellow needles. Anal. Calcd for $C_8H_{24}N_7Cl_2O_{12}Co$ (cis isomer): C, 17.79; H, 4.48; N, 18.16; Cl, 13.13. Found: C, 17.6; H, 4.5; N, 18.0; Cl, 13.3. ^1H NMR: δ 6.35, 6.10, 5.34, 5.10 (8 H, br, quar, NH_2), 3.22 (2 H, s, OH_2), 2.78, 2.6 (8 H, CH_2), 2.58 (6 H, s, CH_3) in Me_2SO-d_6. The acetonitrile methyl singlets for the cis and trans isomers are distinctly different. The crude solid isolated (near quantitatively) from reaction of *cis*-$Co(en)_2(OSO_2CF_3)_2^+$ in acetonitrile gave a single methyl signal coincident with that of authentic *cis*-$Co(en)_2(NCCH_3)_2^{3+}$.

4. Kinetic Measurements. Kinetics of aquation were determined by using a Cary 118C recording spectrophotometer, at 25.0 ± 0.1 °C. Reactions were initiated either by direct dissolution of solid complex in the equilibrated solvent or, for faster runs, by injecting preequilibrated solvent from a reservoir syringe through a mixing chamber containing solid complex on a sintered glass frit directly into the spectrophotometer cell. The progress of reaction can be monitored in the latter method within a few seconds of dissolution. For the presumed acetone and (sulfolane)pentaamminecobalt(III) complexes, reactions were initiated by injecting small volumes of saturated solutions of [$Co(NH_3)_5OSO_2CF_3](CF_3SO_3)_2$ in these solvents directly into a temperature-equilibrated aqueous solution in a cell; the nonaqueous component was maintained at <10% (v/v). Reactions were followed for at least 4 half-lives at suitable wavelengths; rate constants were evaluated by least-squares computer fitting to a single exponential term (for first-order processes) or by graphical separation (for those reactions showing consecutive first-order processes).[15] The rate constants given are the mean values obtained from three or more identical experiments.

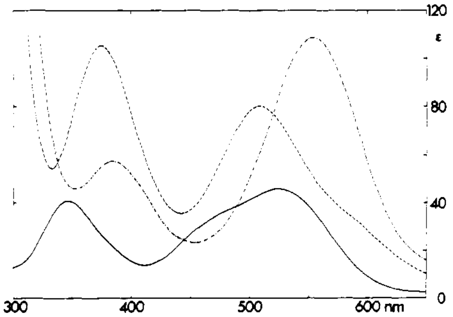

Figure 1. Visible absorption spectra of $Co(NH_3)_5(OSO_2CF_3)^{2+}$ (—), *cis*-$Co(en)_2(OSO_2CF_3)_2^+$ (---), and *fac*-$Co(dien)(OSO_2CF_3)_3$ (···) in anhydrous trifluoromethanesulfonic acid.

Results and Discussion

Syntheses and Characterization. (Triflato)pentaamminecobalt(III) triflate was isolated as a purple solid and proved to be stable for long periods if stored in a closed container; exposure to atmospheric moisture led to slow deterioration. The recrystallized complex shows absorption maxima at 524 nm (ϵ_{524} 45.8 M^{-1} cm^{-1}), 465 nm (sh, ϵ_{465} 32.6 M^{-1} cm^{-1}) and 343 nm (ϵ_{343} 40.0 M^{-1} cm^{-1}), recorded in anhydrous CF_3SO_3H at room temperature (Figure 1). The infrared spectrum of the complex (freshly prepared KBr disk) exhibited bands not present in [$Co(NH_3)_5Br](CF_3SO_3)_2$ or KO_3SCF_3, which arise as a result of nonequivalent absorption for coordinated and ionic $CF_3SO_3^-$ (e.g., at 1350 and 1270 cm^{-1}, respectively). Ionic trifluoromethanesulfonate ion was also identified in the ^{13}C NMR spectra of (amine)cobalt(III) complexes as a low-intensity ^{13}C–^{19}F-coupled quartet (1:3:3:1 peak intensity ratio, coupling constant 318 Hz) centered 53.0 ppm downfield from dioxane (internal reference) in D_2O. The $Co(NH_3)_5OSO_2CF_3^{2+}$ ion hydrolyzes rapidly in both acidic (k = 0.027 s^{-1}, 25 °C, μ = 1.0 M) and basic solution ($k_{OH} \geq 10^6$ M^{-1} s^{-1}, 25 °C, μ = 1.0 M), yielding only aquapentaamminecobalt(III) ion in the absence of competing anions, with exclusive cobalt–oxygen bond cleavage.[7]

A number of alternative methods for the preparation of labile cobalt(III) complexes for use as synthetic precursors have appeared. Nitrosation of azidopentaamminecobalt(III) in solvent media[16] evidently produced complexes containing the coordinated solvent by way of a $Co(NH_3)_5^{3+}$ intermediate (eq 1).[17] Solvent, added anion (Y^-), or added ligand may

$$Co(NH_3)_5N_3^{2+} + NO^+ \rightarrow [Co(NH_3)_5^{3+}]^* + N_2 + N_2O \xrightarrow[Y^{n-}]{\text{solvent}} Co(NH_3)_5(\text{solvent})^{3+} + Co(NH_3)_5Y^{m+} \quad (1)$$

compete for the vacant coordination site. This reaction carried out in concentrated aqueous $HClO_4$ or in CF_3SO_3H yields $Co(NH_3)_5OClO_3^{2+}$ and $Co(NH_3)_5OSO_2CF_3^{2+}$, respectively.[6,7] Reactions in sulfolane and methyl acetate apparently gave labile complexes containing the coordinated solvents.[18] Substitution of coordinated dimethyl sulfoxide[19] or trialkyl phosphate[14,17] by other ligands in solutions of $Co(NH_3)_5OP(OR)_3^{3+}$ or $Co(NH_3)_5OS(CH_3)_2^{3+}$ in suitable solvents has also been employed, but since these complexes are considerably more inert than $Co(NH_3)_5OSO_2CF_3^{2+}$, their usefulness is more limited. Chlorine oxidation of coordinated Me_2SO in solution also generates a good leaving group;[6] competition for the pentacoordinate intermediate can then occur. Alkylation of

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(16) Jordan, R. B.; Sargeson, A. M.; Taube, H. *Inorg. Chem.* **1966**, *5*, 1091.

(17) See, for example: Jackson, W. G.; Lawrance, G. A.; Sargeson, A. M. *Inorg. Chem.* **1980**, *19*, 1001 and references therein.

(18) Hurst, J. K.; Taube, H. *J. Am. Chem. Soc.* **1968**, *90*, 1174.

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Table I. Visible Absorption Maxima of (Amine)cobalt(III) Complexes[a]

complex	λ_{max}, nm (ϵ_{max}, M^{-1} cm^{-1})
$Co(NH_3)_5OSO_2CF_3^{2+}$	524 (45.8), 465 sh (33), 345 (40.6)[b]
$Co(NH_3)_5OH_2^{3+}$	492 (47.5), 346 (44.5)[c]
$Co(NH_3)_6^{3+}$	475 (56.7), 339 (45.8)[d]
$Co(NH_3)_5OHC_2H_5^{3+}$	497 (48.7), 346 (47.6)
$Co(NH_3)_5OHCH_3^{3+}$	498.5 (47.9), 346.5 (47.2)[e]
$Co(NH_3)_5OHCH(CH_3)_2^{3+}$	494 (48.8), 345 (50.2)
$Co(NH_3)_5OS(CH_3)_2^{3+}$	518 (60.2), 351 (60.8)[f]
$Co(NH_3)_5NCCH_3^{3+}$	467 (62.5), 335 (54.0)[g]
$Co(NH_3)_5OCH{\cdot}N(CH_3)_2^{3+}$	506 (77.6), 348 (65.6)[h]
$Co(NH_3)_5OP(OCH_3)_3^{3+}$	517.5 (49.3), 470 sh (36.7), 347 (39.6)[i]
$Co(NH_3)_5OC(NH_2)_2^{3+}$	517 (79.0), 351.5 (59.7)[j]
$Co(NH_3)_5NCNH_2^{3+}$	480 (75.6), 340 (66.1)[k]
$Co(NH_3)_5OOCCH_3^{2+}$	502 (75.2), 352 (59.0)
$Co(NH_3)_5OOCCHCl_2^{2+}$	502 (71.2), 350 (56.0)
$Co(NH_3)_5OC(CH_3)_2^{3+}$	518 (53.0), 468 sh (39), 348 sh (46)[l]
$Co(NH_3)_5O_2SC_4H_8^{3+}$	523 (50.8), 465 sh (37), 346 (45),[m] 517 (52), 465 sh (42), 340 sh (86)[n]
cis-$Co(en)_2(OSO_2CF_3)_2^{+}$	590 sh (33), 508 (80.1), 374 (105.3)[b]
cis-$Co(en)_2(OHCH_3)_2^{3+}$	493 (80.0), 359 (64.8)
cis-$Co(en)_2(OS(CH_3)_2)_2^{3+}$	509.5 (116.3), 371 (96.4)[o]
cis-$Co(en)_2(NCCH_3)_2^{3+}$	456 (102.1), 335 (86.0)
trans-$Co(en)_2(NCCH_3)_2^{3+}$	446.5 (69.3), 350 sh (54.8)
fac-$Co(dien)(OSO_2CF_3)_3$	553 (108.5), 385 (57.3)[b]

[a] Measured in aqueous solution unless specified. The salts of the complexes used are those reported in the Experimental Section. [b] Measured in anhydrous trifluoromethanesulfonic acid as the $CF_3SO_3^-$ salt. [c] Lit.[22] 492 (47.9) in 1 M $NaClO_4$, pH 5. [d] Lit.[22] 479 (57.6) in 3 M HCl. [e] Lit.[16] 494 (49), 345 (50). [f] Lit.[19] 515, 352 in Me_2SO. [g] Lit.[16] 465 (57), 330 (53). [h] Lit.[23] 505 (76), 347 (62.5). [i] Lit.[23] 515 (46.3), 345 (39.3). [j] Lit.[14] 514 (78.9), 350 (60.3). [k] Measured in 1.02 M $HClO_4$. Lit.[21] 480 (73.7), 339 (65.3) in 1 M $HClO_4$. [l] Prepared as a solution of $[Co(NH_3)_5OSO_2CF_3](CF_3SO_3)_2$ in acetone. [m] Prepared as a solution of $[Co(NH_3)_5OSO_2CF_3](CF_3SO_3)_2$ in sulfolane. [n] Prepared as a solution of $[Co(NH_3)_5OClO_3](ClO_4)_2$ in sulfolane. [o] Lit.[30] 510 (112).

Table II. Rate Constants for the Aquation of (Amine)cobalt(III) Complexes at 25.0 °C

complex	*k*, s^{-1}	ref
$Co(NH_3)_5OClO_3^{2+}$	1.0×10^{-1} [a]	32
$Co(NH_3)_5OSO_2CF_3^{2+}$	$2.6_8 \times 10^{-2}$ [b]	*c*
$Co(NH_3)_5OSO_2F^{2+}$	2.2×10^{-2} [d]	32
$Co(NH_3)_5OH_2^{3+}$	5.9×10^{-6} [d,e]	32
$Co(NH_3)_5OHCH_3^{3+}$	$5.9_5 \times 10^{-5}$ [b]	*c*
$Co(NH_3)_5OHC_2H_5^{3+}$	$7.6_5 \times 10^{-5}$ [b]	*c*
$Co(NH_3)_5OHCH(CH_3)_2^{3+}$	$3.5_0 \times 10^{-4}$ [b]	*c*
$Co(NH_3)_5OP(OCH_3)_3^{3+}$	2.5×10^{-4} [f]	32
$Co(NH_3)_5OS(CH_3)_2^{3+}$	2.2×10^{-5} [g,h]	32
$Co(NH_3)_5OCH{\cdot}N(CH_3)_2^{3+}$	1.5×10^{-6} [d,h]	32
$Co(NH_3)_5OC(NH_2)_2^{3+}$	4.0×10^{-5} [a]	*c*
$Co(NH_3)_5OC(CH_3)_2^{3+}$	4.1×10^{-2} [b,i]	*c*
$Co(NH_3)_5O_2SC_4H_8^{3+}$	3.1×10^{-2} [b,i]	*c*
$Co(NH_3)_5O_2CCH_3^{2+}$	2.7×10^{-8} [h,j]	32
$Co(NH_3)_5O_2CCHCl_2^{2+}$	1.5×10^{-7} [h,j]	32
$Co(NH_3)_6^{3+}$	5.8×10^{-12} [f,h]	32
$Co(NH_3)_5(OSO_2CH_3)^{2+}$	2.0×10^{-4} [d]	32
cis-$Co(en)_2(OSO_2CF_3)_2^{+}$	2.2×10^{-2}, 8.6×10^{-3} [b,k]	*c*
cis-$Co(en)_2Cl_2^{+}$	2.4×10^{-4},[l] 1.6×10^{-6} [j]	33
fac-$Co(dien)(OSO_2CF_3)_3$	4.0×10^{-2}, 1.1×10^{-2}, 4.0×10^{-3} [b,k]	*c*

[a] Measured in 1.0 M $HClO_4$. [b] Measured in 0.1 M CF_3SO_3H. [c] This work. [d] Measured in 0.01 M $HClO_4$. [e] Self-exchange. [f] Measured in 0.1 M $HClO_4$. [g] Measured in 10^{-3} M $HClO_4$. [h] Calculated by extrapolation of reported data to 25 °C. [i] Measured as described in the text. [j] pH-independent rate constant. [k] Approximate rate constants determined by graphical separation of consecutive first-order processes. [l] Measured in 0.01 M HNO_3.

the carbonyl oxygen in (acetato)pentaamminecobalt(III) produced a coordinated ester which is also an excellent leaving group.[20] If the alkylation is carried out in a coordinating solvent, a complex of the solvent is produced.

The synthetic advantages of reacting a well-characterized, isolated complex, rather than competing for an intermediate generated in situ, are evident. Dissolution of $Co(NH_3)_5OSO_2CF_3^{2+}$ directly in a range of solvents produces the pure solvent complexes quantitatively. An analytically pure sample can usually be obtained by evaporation of the solvent at reduced pressure or by precipitation with diethyl ether. However, we have not been able to isolate analytically pure solid samples of the acetone or sulfolane complexes. Visible spectra of $Co(NH_3)_5OSO_2CF_3^{2+}$ in both solvents do not differ markedly from that recorded in CF_3SO_3H (Table I), although the aquation rates (especially for the acetone solvate) differ from that of $Co(NH_3)_5OSO_2CF_3^{2+}$ (Table II). For the putative sulfolane complex, this latter difference could merely reflect differences in solvent composition (~10% sulfolane in 0.1 M CF_3SO_3H vs. 0.1 M CF_3SO_3H). Previously reported preparations of (sulfolane)pentaamminecobalt(III),[18,20] which has never been characterized as a solid sample, have been carried out in the presence of poorly coordinating anions (i.e., ClO_4^-, $CF_3SO_3^-$), and the possibility that the product is merely a solution of $Co(NH_3)_5OClO_3^{2+}$ or $Co(NH_3)_5OSO_2CF_3^{2+}$ in sulfolane cannot be excluded. We attempted to resolve this problem by examining also the visible spectrum of $[Co(NH_3)_5OClO_3](ClO_4)_2$ in sulfolane. Although similar, the spectrum was not identical with the spectrum of $Co(NH_3)_5OSO_2CF_3^{2+}$ in sulfolane. The visible spectrum of the authentic perchlorato complex[7] in $HClO_4$ (12 M) was not accessible because the solubility was too low. Also, we were unable to measure the aquation rate of samples of the perchlorato complex after dissolution in sulfolane because of the very limited solubility of $[Co(NH_3)_5OClO_3](ClO_4)_2$ in that solvent. The limited results are more consistent with the presence of the ions $Co(NH_3)_5OClO_3^{2+}$ and $Co(NH_3)_5OSO_2CF_3^{2+}$ in sulfolane rather than a discrete sulfolane complex.

A strong case can however be made for the existence of (acetone)pentaamminecobalt(III).[18] Freeze-drying of an acetone solution of $[Co(NH_3)_5OSO_2CF_3](CF_3SO_3)_2$ produced a red solid which reverted to the violet starting material on prolonged vacuum-drying at room temperature. The [^{1}H] NMR spectrum (60 MHz) of a fresh solution of the red complex in Me_2SO-d_6 showed two acetone resonances separated by ~8 Hz. After 10 min, only one signal corresponding to free acetone remained, consistent with the observed lability of the acetone complex (Table II).

The reactivity of sulfolane and acetone solutions of $Co(NH_3)_5(OSO_2CF_3)^{2+}$ toward ligand substitution makes these solvents ideal for reactions where the required ligand is a neutral solid. Simple, high-yielding syntheses of pentaamminecobalt(III) complexes of urea and cyanamide from reaction of $Co(NH_3)_5OSO_2CF_3^{2+}$ with the ligands in sulfolane illustrate this procedure. Previously reported routes to these complexes required vigorous conditions and involved tedious fractional recrystallizations to obtain products in lower yields.[14,21] Further, nitrosation of $Co(NH_3)_5N_3^{2+}$ in sulfolane in the presence of urea or cyanamide is not a feasible synthetic route since the ligands are themselves susceptible to nitrosation. Reactions in sulfolane or acetone with anionic ligands as their lithium or tetraalkylammonium salts may be complicated by the immediate precipitation of $Co(NH_3)_5OSO_2CF_3^{2+}$ by the added anion. However, reaction may still proceed on prolonged

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(20) Jackman, L. M.; Dormish, J. F.; Scott, R. M.; Portman, R. H.; Minarol, R. D. *Inorg. Chem.* **1979**, *18*, 1503.

(21) Balahura, R. J.; Jordan, R. B. *J. Am. Chem. Soc.* **1971**, *93*, 625.

(22) Buckingham, D. A.; Francis, D. J.; Sargeson, A. M. *Inorg. Chem.* **1974**, *13*, 2630.

stirring or warming of the suspension. A more successful preparation of acidopentaamminecobalt(III) complexes by dissolution of $[Co(NH_3)_5OSO_2CF_3](CF_3SO_3)_2$ in neat liquid acids containing a small amount of base has been developed and is illustrated by the preparation of the acetato and dichloroacetato complexes.

The precursor $Co(NH_3)_5OSO_2CF_3^{2+}$ ion and the range of complexes prepared by ligand substitution have been characterized spectrophotometrically, by NMR spectroscopy and by microanalysis. While many of the derivatives have been prepared previously by other routes,[23] the procedures have sometimes been lengthy and the purity of the product has often been unsatisfactory. Visible absorption maxima of all of the complexes prepared are given in Table I; each complex exhibits two characteristic ligand field bands. The effective C_{4v} symmetry of the ions $Co(NH_3)_5OSO_2CF_3^{2+}$, $Co(NH_3)_5OC(CH_3)_2^{3+}$, and $Co(NH_3)_5OP(OCH_3)_3^{3+}$ is reflected in the asymmetry of the first ligand field envelope (Table I and Figure 1) where the $^1A_1 \rightarrow {}^1E$ and $^1A_1 \rightarrow {}^1A_2$ component transitions are evident.

For illustration of the extension of these preparative procedures to other (amine)cobalt(III) systems,[24] syntheses of $Co(en)_2(OSO_2CF_3)_2^+$ and $Co(dien)(OSO_2CF_3)_3$ were developed. Visible absorption spectra of these complexes are compared with that of the pentaamminecobalt(III) complex in Figure 1. As discussed below, the bis(ethylenediamine)cobalt(III) complex has the cis configuration, while the (diethylenetetramine)cobalt(III) complex is presumed to have a predominantly *fac* configuration.

The product of the reaction of either *cis*- or *trans*-$Co(en)_2Cl_2^+$ with anhydrous CF_3SO_3H was *cis*-$[Co(en)_2(OSO_2CF_3)_2](CF_3SO_3)$. This is consistent with the cis complexes being more stable in polar solvents than the trans isomers.[25] Absorption spectra (in H_2O as $Co(en)_2(OH_2)(OH)^{2+}$) of the aquation product of $Co(en)_2(OSO_2CF_3)_2^+$ of either origin are consistent with 94 ± 2% cis isomer in each case, and the solvolysis products in Me_2SO-d_6 have ^1H NMR spectra identical with that of an authentic sample of *cis*-$Co(en)_2(OSMe_2)_2^{3+}$. Regardless of whether the bis(triflato) complex was prepared from *cis*- or *trans*-$Co(en)_2Cl_2^+$, the yellow bis(acetonitrile) complex isolated from reaction in acetonitrile exhibits a ^1H NMR spectrum identical with that of authentic *cis*-$Co(en)_2(NCCH_3)_2^{3+}$. Both cis and trans isomers of the bis(acetonitrile) complex have been prepared by other synthetic routes,[26] and their NMR spectra are different. Reaction of *cis*-$Co(en)_2(OSO_2CF_3)_2^+$ in dimethyl sulfoxide or acetonitrile to form complexes containing the coordinated solvents was moderately slow; in the latter solvent, a color change from purple to red to yellow was observed over $\sim {}^1/_2$ h at 25 °C. Consequently, the ^1H NMR spectrum of a freshly prepared solution in Me_2SO-d_6 is essentially that of the bis(triflato) complex. The observation of a pattern for the amine protons analogous to both that of the final product and that of a range of *cis*-$Co(en)_2X_2^{n+}$ complexes[27] supports the assignment of a cis configuration, and precludes the possibility that isomerization during substitution accounts for the final observations.

Initially, the expected outcome of reacting $Co(en)_2CO_3^+$ with anhydrous CF_3SO_3H was the production of the synthetically useful $Co(en)_2(OH_2)(OSO_2CF_3)^{2+}$ complex. Liberation of CO_2 from the carbonate complex was expected to proceed with cleavage of one cobalt–oxygen and one carbon–oxygen bond, leaving one cobalt–oxygen bond intact. Unfortunately, the product isolated from this reaction proved to be *cis*-$Co(en)_2(OSO_2CF_3)_2$; apparently the coordinated water in the presumed $Co(en)_2(OH_2)(OSO_2CF_3)^{2+}$ intermediate is readily abstracted (perhaps as H_3O^+) in the strongly acidic solution, even when the reaction is carried out at −5 °C. When chiral $Co(en)_2CO_3^+$ was used as precursor, the product isolated was racemic. In water, this product exhibited the absorption spectrum of *cis*-$Co(en)_2(OH)(OH_2)^{2+}$, and both this solution and one of regenerated $Co(en)_2CO_3^+$ [28] showed a retention of chirality of less than 1%. We have not determined the stage or stages at which chirality is lost, but it could occur at the initial cleavage of CO_2 and/or at the substitution of the second $CF_3SO_3^-$ ion.

There is some evidence to support the apparent rapid anation of the presumed intermediate *cis*-$Co(en)_2(OH_2)(OSO_2CF_3)^{2+}$. We have observed that $Co(NH_3)_5OCO_2^+$ decomposes in triflic acid to give initially $Co(NH_3)_5(OH_2)^{3+}$ which on standing at 25 °C yields $Co(NH_3)_5OSO_2CF_3^{2+}$ within ~10 min. The water-exchange rate of $Co(NH_3)_5(OH_2)^{3+}$ and cis ⇌ trans isomerization rate of $Co(en)_2(OH_2)_2^{3+}$ are acid catalyzed, the rate enhancement being ~10-fold in 3 M $HClO_4$.[29] Since the uncatalyzed $Co(en)_2(OH_2)_2^{3+}$-exchange rate with water is faster than that for the pentaammine complex and in turn the estimated water-exchange rates for *cis*-$Co(en)_2X(OH_2)_2^+$ ions are faster than the rate for *cis*-$Co(en)_2(OH_2)_2^{3+}$,[29] it is not unreasonable that *cis*-$Co(en)_2(OSO_2CF_3)(OH_2)^{2+}$ should be anated rapidly by $CF_3SO_3^-$ via an acid-catalyzed path in neat CF_3SO_3H.

The absence of lattice or coordinated water in the product from the $Co(en)_2CO_3^+$ reaction was established by elemental analysis, by ^1H NMR spectrometry and from its reactivity toward solvolysis in Me_2SO. In dry Me_2SO-d_6, the ^1H NMR spectrum changed (~5 min) to that of the known[30] *cis*-$Co(en)_2(Me_2SO)_2^{3+}$. The initial, intermediate, and final spectra showed the four broad NH_2 resonances characteristic of the cis topology, and peaks attributable to lattice or bound water were absent. These results are consistent with a two-step solvolysis reaction which proceeds largely with retention of the cis configuration. The known[30] *cis*-$Co(en)_2(OH_2)(Me_2SO)^{3+}$ ion does not solvolyze to *cis*-$Co(en)_2(Me_2SO)_2^{3+}$ in the time scale of the present reaction, and the nearly quantitative isolation of *cis*-$Co(en)_2(Me_2SO)_2^{3+}$ from such a reaction is consistent with the absence of *cis*-$Co(en)_2(OH_2)(OSO_2CF_3)^{2+}$ ion as the product of the $Co(en)_2CO_3^+ + CF_3SO_3H$ reaction. This reaction is a particularly facile route to the *cis*-$Co(en)_2(OSO_2CF_3)_2^+$ complex.

The neutral $Co(dien)(OSO_2CF_3)_3$ complex was prepared as an example of a complex containing three trifluoromethanesulfonate ligands. The product is presumed to have

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(23) Preparations of the following $Co(NH_3)_5L^{n+}$ complexes have been described previously. L = OH_2: Diel, H.; Clark, H.; Willard, H. H. *Inorg. Synth.* **1939**, *1*, 186. L = NH_3: Bjerrum, J.; McReynolds, J. P. *Ibid.* **1946**, *2*, 216. L = OHC_2H_5: Borghi, E.; Monacelli, F. *Inorg. Chim. Acta* **1977**, *23*, 53. L = $OHCH_3$: ref 16. L = $OS(CH_3)_2$: ref 19. L = $NCCH_3$: ref 16. L = $OCH{\cdot}N(CH_3)_2$: Gould, E. S. *J. Am. Chem. Soc.* **1965**, *87*, 4730. L = $OP(OCH_3)_2$: Dolbear, G. E.; Taube, H. *Inorg. Chem.* **1967**, *6*, 60. L = $OC(NH_2)_2$: ref 14. L = $NCNH_2$: ref 21. L = O_2CCH_3: Basolo, F.; Murmann, R. K. *Inorg. Synth.* **1953**, *4*, 171. L = O_2CCHCl_2: Basolo, F.; Bergmann, J. G.; Pearson, R. G. *J. Phys. Chem.* **1952**, *56*, 22.

(24) The rhodium(III) analogue $[Rh(NH_3)_5OSO_2CF_3](CF_3SO_3)_2$ has been prepared from $[Rh(NH_3)_5Cl]Cl_2$ by an analogous procedure and used as a precursor for several pentaamminerhodium(III) complexes: Dixon, N. E.; Sargeson, A. M., unpublished results.

(25) Jackson, W. G.; Fee, W. W. *Inorg. Chem.* **1975**, *14*, 1161 and references therein.

(26) Based on nitrosation in acetonitrile of *cis*- or *trans*-$[Co(en)_2(N_3)_2](ClO_4)$ prepared by the methods of: Buckingham, D. A.; Olsen, I. I.; Sargeson, A. M. *Inorg. Chem.* **1967**, *6*, 1807. Staples, P. J.; Tobe, M. L. *J. Chem. Soc.* **1960**, 4803, 4812 (see Experimental Section for details).

(27) See, for example: Buckingham, D. A.; Durham, L.; Sargeson, A. M. *Aust. J. Chem.* **1967**, *20*, 257.

(28) Prepared by reaction of the product in bicarbonate solution and crystallized as the perchlorate salt.

(29) Kruse, W., Taube, H. *J. Am. Chem. Soc.* **1961**, *83*, 1280. Hunt, H. R.; Taube, H. *J. Am. Chem. Soc.* **1958**, *80*, 2642.

(30) Jackson, W. G.; Sargeson, A. M. *Inorg. Chem.* **1978**, *17*, 1348.

predominantly the *fac* configuration, since this is the stereochemistry of the rapidly generated aquation product.[12,31] The absorption spectrum in CF_3SO_3H (Figure 1) shows symmetric bands with maxima (553, 385 nm) more comparable with *fac*-$Co(dien)(OH_2)_3^{3+}$ (520, 365 nm) than with *mer*-$Co(dien)(OH_2)_3^{3+}$ (480, 385 nm). The first ligand field band of *fac*-$Co(dien)(OH_2)_3^{3+}$ is also symmetric, while that of the *mer* isomer is asymmetric.[31] The possibility that a small percentage of *mer*-$Co(dien)(OSO_2CF_3)_3$ exists in our product cannot, however, be excluded.

Kinetic Measurements. (Triflato)pentaamminecobalt(III) ion aquates in acidic solution at a rate similar to that for (fluorosulfonato)pentaamminecobalt(III), and only 3 times more slowly than (perchlorato)pentaamminecobalt(III) (Table II). Rate constants for the aquation of a range of pentaamminecobalt(III) complexes which have been previously reported[32] or determined in this study are given in Table II. The lability of the putative sulfolane and acetone complexes accounts for their suitability as solvents for substitution reactions with other ligands. Acetone is a better leaving group than dimethyl sulfoxide by a factor of ~2000, in spite of their apparent structural similarity. The kinetic inertness of the alcohol complexes deserves comment. For the pentaamminecobalt(III) complexes, a ratio of aquation rate constants of 1:10:13:60 is observed for the complexes of OH_2, $OHCH_3$, $OHCH_2CH_3$, and $OHCH(CH_3)_2$, respectively (Table II). The aquation of $Co(NH_3)_5OHCH_3^{3+}$ is only 1 order of magnitude faster than the self-exchange of water in $Co(NH_3)_5OH_2^{3+}$, and the structure of the coordinated alcohol has little effect on the rate constants.

Hydrolysis of *cis*-$Co(en)_2(OSO_2CF_3)_2^+$ in 0.1 M CF_3SO_3H occurs as two rapid consecutive first-order processes (eq 2).

$$\textit{cis}\text{-}\mathrm{Co(en)_2(OSO_2CF_3)_2^+} \xrightarrow{k_1} \textit{cis}\text{-}\mathrm{Co(en)_2(OSO_2CF_3)(OH_2)^{2+}} \xrightarrow{k_2} \textit{cis}\text{-}\mathrm{Co(en)_2(OH_2)_2^{3+}} \quad (2)$$

Within seconds of dissolution the aquation of $Co(en)_2(OSO_2CF_3)_2^+$ showed significant curvature in the log $|A_t - A_\infty|$ vs. time plots. This behavior was consistent with two consecutive rate processes. Care was exercised in the experimental procedure so that the curvature could not be attributed to schlieren effects or changing temperature. Moreover, the rates for the two processes have been reproduced by using absorbance data collected at different wavelengths on different spectrophotometers. It has been pointed out elsewhere[15] that it is not possible to decide a priori which step, the first or second, is the faster. However, several lines of evidence support a fast–slow assignment. First, the rate constants correspond closely with the purely statistical expectation, $k_1 = 2k_2$. Second and more convincingly, given $k_1 = 2k_2$, the calculated ϵ, at several wavelengths, for the intermediate species *cis*-$Co(en)_2(OH_2)(OSO_2CF_3)^{2+}$ is more chemically reasonable. By analogy with similar systems the spectrum of the intermediate should be close to the average of the precursor and final spectra. The alternate rate constant assignment $k_2 \simeq 2k_1$ does not lead to this result. Furthermore, the observation of isosbestic points at 482.5 (ϵ 72.9), 423.5 (ϵ 17.3), 362.5 (ϵ 59.4), and 314.5 nm (ϵ 16.4) obtained for times as early as 20% reaction is compatible only with an intermediate having closely the average spectrum of reactant and final product.

Determined rate constants (25 °C, $\mu = 0.1$ M) were 2.2 ($\pm$0.2) $\times 10^{-2}$ s^{-1} (k_1) and 8.6 ($\pm$0.5) $\times 10^{-3}$ s^{-1} (k_2). This behavior differs from that generally observed for $Co(en)_2X_2^{n+}$ complexes, where $k_2 \ll k_1$ (e.g., for X = Cl, $k_1/k_2 = 150$,[33] but $k_1/k_2 = 2.6$ for X = OSO_2CF_3). The absorption spectrum of the final hydrolysis product in 0.1 M CF_3SO_3H was predominantly (94 ± 2%) *cis*-$Co(en)_2(OH_2)_2^{3+}$, indicating that the reaction proceeds with essentially complete retention of the cis configuration. This is not unreasonable since aquation is rapid, and cis $\rightleftharpoons$ trans equilibria of $Co(en)_2X(OH_2)^{n+}$ complexes are usually established relatively slowly.

The kinetics of aquation of $Co(dien)(OSO_2CF_3)_3$ are complex, since at least three consecutive first-order steps are available, excluding isomerization reactions. Although accurate kinetic study is precluded both by this complexity and by the limited solubility of the neutral tris(triflato) complex, at least three rapid sequential reactions are separable graphically[15] (Table II), although assignment of a fast–slow–slower process is necessarily arbitrary. The final aquation product is predominantly (≥98%) *fac*-$Co(dien)(OH_2)_3^{3+}$, determined spectrophotometrically.[31] The product elutes as a single band from columns of SP-Sephadex C-25 (tartrate buffer eluant) and Dowex 50W × 2 (HCl eluant), under conditions where *mer*- and *fac*-$Co(dien)(OH_2)_3^{3+}$ are separable. Under basic conditions, hydrolysis is extremely rapid, producing a purple solution of *mer*-$Co(dien)(OH)_3$ which upon acidification forms the orange *mer*-$Co(dien)(OH_2)_3^{3+}$ (identified spectrophotometrically[31]). Since the stereochemistry of the $Co(dien)(OSO_2CF_3)_3$ complex is presumed to be *fac* (discussed above), base hydrolysis appears to occur with isomerization, while aquation proceeds with retention of stereochemistry. The earlier observation that isomerization of *fac*- → *mer*-$Co(dien)(OH_2)_3^{3+}$ is very slow in acidic solution[31] implies that the rapid acid aquation of $Co(dien)(OSO_2CF_3)_3$ proceeds stereoretentively, consistent with our assignment of *fac* geometry to this complex.

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Registry No. $[Co(NH_3)_5OSO_2CF_3](CF_3SO_3)_2$, 75522-50-8; *cis*-$[Co(en)_2(OSO_2CF_3)_2](CF_3SO_3)$, 75522-52-0; $Co(dien)(OSO_2CF_3)_3$, 75522-53-1; $[Co(NH_3)_5OH_2](ClO_4)_3$, 13820-81-0; $[Co(NH_3)_5](ClO_4)_3$, 13820-83-2; $[Co(NH_3)_5OHCH_2CH_3](CF_3SO_3)_3$, 75522-54-2; $[Co(NH_3)_5OHCH_3](CF_3SO_3)_3$, 75522-55-3; $[Co(NH_3)_5OHCH(CH_3)_2](CF_3SO_3)_3$, 75522-57-5; $[Co(NH_3)_5NCCH_3](ClO_4)_2(CF_3SO_3)$, 75522-58-6; $[Co(NH_3)_5OP(OCH_3)_3](ClO_4)_3$, 15041-41-5; $[Co(NH_3)_5OCH{\cdot}N(CH_3)_2](CF_3SO_3)_3$, 75522-59-7; $[Co(NH_3)_5OS(CH_3)_2](CF_3SO_3)_3$, 75522-60-0; $[Co(NH_3)_5OC(NH_2)_2](S_2O_6)_{3/2}$, 75522-61-1; $[Co(NH_3)_5OC(NH_2)_2](ClO_4)_3$, 27427-53-8; $[Co(NH_3)_5NCNH_2](ClO_4)_3$, 75557-17-4; $[Co(NH_3)_5(OOCCH_3)](ClO_4)_2$, 14523-28-5; $[Co(NH_3)_5(OOCCHCl_2)](ClO_4)_2$, 14096-70-9; *cis*-$[Co(en)_2(HOCH_3)_2](CF_3SO_3)_3$, 75522-63-3; *cis*-$[Co(en)_2(Me_2SO)_2](ClO_4)_3$, 14781-36-3; *cis*-$[Co(en)_2(NCCH_3)_2](NO_3)(ClO_4)_2$, 75522-65-5; *trans*-$[Co(en)_2(NCCH_3)_2](ClO_4)_3$, 75557-19-6; $[Co(NH_3)_5Cl]Cl_2$, 13859-51-3; *cis*-$[Co(en)_2Cl_2]Cl$, 14040-32-5; *trans*-$[Co(en)_2Cl_2]Cl$, 14040-33-6; $[Co(en)_2CO_3]Cl$, 15842-50-9; *cis*-$[Co(en)_2(OSO_2CF_3)_2](ClO_4)$, 75522-66-6; $Co(dien)Cl_2$, 14215-59-9; $Co(NH_3)_5OS(CD_3)_2^{3+}$, 75522-67-7; *cis*-$[Co(en)_2(N_3)_2](ClO_4)$, 14877-87-3; *trans*-$[Co(en)_2(N_3)_2](ClO_4)$, 14781-34-1; $Co(NH_3)_5OC(CH_3)_2^{3+}$, 75522-68-8; $Co(NH_3)_5O_2SC_4H_8^{3+}$, 46145-85-1; $[Co(NH_3)_5OP(OCH_3)_3](CF_3SO_3)_3$, 75522-69-9; $^{17}OH_2$-labeled $[Co(NH_3)_5OH_2](CF_3SO_3)_3$, 75522-71-3.

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(31) Caldwell, S. H.; House, D. A. *J. Inorg. Nucl. Chem.* **1969**, *31*, 811.

(32) Rate constants for the aquation of $Co(NH_3)_5L^{n+}$ complexes not determined in this work appear in the following sources. L = $OClO_3$: ref 6. L = OSO_2F: Jackson, W. G., unpublished data. L = OH_2 (self-exchange): Hunt, H. R.; Taube, H. *J. Am. Chem. Soc.* **1958**, *80*, 2642. L = $OP(OCH_3)_3$: Schmidt, W.; Taube, H. *Inorg. Chem.* **1963**, *2*, 698. L = $OS(CH_3)_2$: Reynolds, W. L.; Birus, M.; Asperger, S. *J. Chem. Soc., Dalton Trans.* **1974**, 716. L = $OCH{\cdot}N(CH_3)_2$: Reynolds, W. L.; Knoll, M. A. *Int. J. Chem. Kinet.* **1976**, *8*, 389. L = O_2CCH_3: Monacelli, F.; Basolo, F.; Pearson, R. G. *J. Inorg. Nucl. Chem.* **1962**, *24*, 1241. L = O_2CCHCl_2: ref 23. L = NH_3: Newton, A. M.; Swaddle, T. W. *Can. J. Chem.* **1974**, *52*, 2751. L = OSO_2CH_3: ref 7.

(33) Chan, S. C. *J. Chem. Soc.* **1963**, 5137. Chan, S. C. *Ibid.* **1965**, 418.