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Intramolecular Hydration of Nitriles Coordinated to Cobalt(III). Formation of Five- and Six-Membered Chelated Amides

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Treatment of *cis*-$[Co(en)_2(NH_2CH_2CN)X]^{2+}$ ions (X = Cl, Br) with Hg^{2+} results in the formation of both $[Co(en)_2(glyNH_2)]^{3+}$ and $[Co(en)_2(NH_2CH_2CONH)]^{2+}$ with the product ratio depending on the leaving group; similar treatment of *cis*-$[Co(en)_2(NH_2CH_2CH_2CN)Br]^{2+}$ forms *cis*-$[Co(en)_2(NH_2CH_2CH_2CN)(OH_2)]^{3+}$ initially and $[Co(en)_2(\beta\text{-alaNH}_2)]^{3+}$ finally. Oxidation of *cis*-$[Co(en)_2(NH_2CH_2CN)Br]^{2+}$ with HOCl gives the *cis*-$[Co(en)_2(NH_2CH_2CN)(OH_2)]^{3+}$ ion ($pK_a = 5.60$), and ^{18}O-tracer studies establish that the Hg^{2+}-catalyzed formation of $[Co(en)_2(glyNH_2)]^{3+}$ from *cis*-$[Co(en)_2(NH_2CH_2CN)(^{18}OH_2)]^{3+}$ occurs with retention of the oxygen label. Rate data for the spontaneous hydration of *cis*-$[Co(en)_2(NH_2CH_2CN)(OH_2)]^{3+}$ agree with the rate expression $k_{obsd} = k_1K_a/(K_a + [H^+])$ with $k_1 = 1.15 \times 10^{-2}\ s^{-1}$ ($\Delta H^{\ddagger} = 10.7$ kcal mol^{-1}; $\Delta S^{\ddagger} = -31$ cal $deg^{-1}\ mol^{-1}$) and $pK_a = 5.6$ at 25 °C, $\mu = 1.0$ ($NaClO_4$). The rate law for the Hg^{2+}-catalyzed reactions of *cis*-$[Co(en)_2(NH_2CH_2CN)(OH_2)]^{3+}$ and *cis*-$[Co(en)_2(NH_2CH_2CH_2CN)(OH_2)]^{3+}$ takes the form $k_{obsd} = k_{Hg^{2+}}[Hg^{2+}]/[H^+]$ with $k_{Hg^{2+}} = 0.48$ and $6.5 \times 10^{-5}\ s^{-1}$, respectively. Catalysis by Ag^+ is more complex with the rate data for *cis*-$[Co(en)_2(NH_2CH_2CN)(OH_2)]^{3+}$ agreeing with the expression $k_{obsd} = (k_1'[Ag^+] + k_2'[Ag^+]^2)/[H^+](1 + K_{Ag^+}[Ag^+])$, with $k_1' = 0.8 \times 10^{-3}\ s^{-1}$, $k_2' = 8 \times 10^{-3}\ M^{-1}\ s^{-1}$, and $K_{Ag^+} = 1.3$ M. Catalysis by Zn^{2+}, Hg_2^{2+}, Cd^{2+}, and HPO_4^{2-} is also observed. Full retention of optical configuration obtains in all the reactions.

Introduction

The ability of coordinated water, hydroxide, and amide to act as nucleophiles in intramolecular reactions centered about cobalt(III) has been demonstrated in many instances recently.[1-6] In addition, several examples of the metal-promoted (or -catalyzed) hydration of nitriles to amides have been reported but these studies have involved the solvolysis of the directly coordinated $M\text{–}NCR^{n+}$ moiety.[7-12] This paper reports on the Co(III)-promoted intramolecular hydration of aminoacetonitrile and aminopropionitrile in which the –CN group is not directly bound to the metal center. It reports in detail and extends results given in an earlier communication[13] and subsequently amplified by Nolan and Hay.[14] A following paper will deal with the reaction in neutral and alkaline solutions in which amidine complexes are produced.[25]

Experimental Section

Analytical reagents were used for kinetic measurements without further purification. Aminoacetonitrile hydrogen sulfate was obtained from Adams Chemical Co. or prepared locally.[16,17] Aminoacetonitrile hydrochloride was used in later preparations and was prepared as for the hydrogen sulfate salt using 35% HCl instead of H_2SO_4 and without heating. Anal. Calcd for $C_2N_2H_5Cl$: C, 25.96; H, 5.46; N, 30.28; Cl, 38.31. Found: C, 26.3; H, 5.4; N, 30.2; Cl, 38.3. Aminopropionitrile was purchased from Frinton Laboratories or prepared directly from acrylonitrile.[18] β-Alanine amide hydrobromide was prepared locally from dimedone β-alanine ethyl ester and ammonia.[19] Oxygen-18-enriched water (1.5 atom %) was purchased from Bio-Rad Laboratories. Bio-Rad analytical Dowex 50W-X2 (200–400 mesh) and Sephadex C-25 ion-exchange resins (H^+ form) were used in the analysis of reaction products.

Visible spectra were recorded using a Cary 14 or 118C spectrophotometer. Infrared measurements were made with a Perkin-Elmer 457 spectrophotometer. Optical rotatory power was measured with a Perkin-Elmer P22 spectropolarimeter in a 1-dm tube (±0.002°). ^1H NMR spectra were recorded using Varian HA-100 and JEOLCO Minimar MH-100 spectrometers, with complex concentrations between 0.1 and 0.3 M in deuterated solvents (D_2O, $Me_2SO\text{-}d_6$) with NaTPS or external TMS as references and at 34 or 25 °C, respectively. Atomic absorption determinations for Co were carried out using Varian-Techtron AA4 and AA1000 spectrometers. Determinations of pH were made using a Radiometer TTT 1c pH meter, a pH A 630T scale expander, a G202C glass electrode, and a calomel electrode protected with a NH_4NO_3 (1.6 M)–$NaNO_3$ (0.2 M) salt bridge. The meter was calibrated with 0.05 M potassium hydrogen phthalate (pH 4.01 (25 °C), 4.03 (37 °C), 4.06 (50 °C)) or 0.01 M borax (pH 9.18 (25 °C), 9.09 (37 °C), 9.01 (50 °C)).

Preparation of Complexes. *cis*-$[Co(en)_2Br(NH_2CH_2CN)]Br_2$ was prepared[20] by triturating *trans*-$[Co(en)_2Br_2]Br$ (4.19 g, 0.01 mol), aminoacetonitrile hydrogen sulfate (or aminoacetonitrile hydrochloride) (0.01 mol), and diethylamine (1.03 mL, 0.01 mol), as a paste in methanol. Further, diethylamine (1.03 mL) was slowly added with grinding over 30 min by which time the mixture had turned purple. After alternate grinding and standing for a further 1 h the product was filtered from methanol and air-dried. The product was recrystallized following dissolution in the minimum volume of 0.1 M HBr at ~50 °C and cooling in an ice bath, by the addition of solid NaBr (yield ~40–70%). In some preparations the crude product was purified by dissolution in a large volume of dilute HBr (~0.01 M) and adsorption and elution (1 M NaBr) from Dowex 50W-X2 ion-exchange resin. The purple 2+ band was collected, the volume of the solution was reduced on a rotary evaporator (less than 50 °C) until crystallization of the complex commenced, and then the mixture was cooled in an ice bath. The bromide salt was collected, washed with ethanol, and air-dried (yield ca. 40%). Anal. Calcd for $CoC_6H_{20}N_6Br_3$: Co, 12.41; C, 15.17; H, 4.24; N, 17.70; Br, 50.48. Found (for both methods): Co, 12.6 (12.6); C, 15.2 (15.1); H, 4.3 (4.3); N, 17.4 (17.6); Br, 50.3 (50.5); ϵ_{545} 84 in 0.5 M $HClO_4$–0.5 M $NaClO_4$ at 25.0 °C. *cis*-$[Co(en)_2Br(NH_2CH_2CN)](ClO_4)_2$ was prepared from the above bromide salt by slurrying 4.93 g (0.01 mol) with water (15 mL containing 5 drops of glacial acetic acid), adding silver acetate (3.34 g, 0.02 mol) and shaking rapidly with some glass beads for several minutes. The precipitated AgBr was removed on a Hyflow-supercel filter and washed with 5 mL of dilute $HClO_4$, and the filtrate was treated with several drops of concentrated $HClO_4$. Addition of $NaClO_4$ and cooling in an ice bath produced purple crystals which were removed on a filter and washed with ethanol and air-dried (yield 2.7 g (53%)). Failure to keep the solution sufficiently acidic results in an impure blue-purple product which contains the amidine complex.[15] Smaller quantities of the perchlorate salt were also obtained by dissolving the bromide salt in the minimum volume of warm dilute $HClO_4$, passing the solution through a Dowex 1X8 (200–400 mesh) anion-exchange resin (ClO_4^- form), concentrating the eluent by vacuum evaporation, and adding $NaClO_4$ to the cooled solution. Anal. Calcd for $CoC_6H_{20}N_6O_8Cl_2$: C, 14.02; H, 3.92; N, 16.35; Co, 11.47. Found: C, 14.2; H, 4.1; N, 16.2; Co, 11.7; ϵ_{542} 83 in 0.5 M $NaClO_4$–0.5 M $HClO_4$. The bromide salt (9 g) was resolved by adding sodium (−)-arsenyl tartrate (5.06 g; $[\alpha]_{589}$ −20°) to a warm (45 °C) solution of the complex in dilute HOAc (90 mL of H_2O containing 3–4 drops of glacial HOAc). The diastereoisomer crystallized slowly overnight at 0–10 °C (yield 5.0 g) and addition of further NaAsOtart (2.06 g) and cooling gave an additional fraction (1.77 g) on further standing. All fractions had similar rotations ($[\alpha]_{589}$ −0.110°, $[\alpha]_{436}$ 0.209°) and recrystallization of the diastereoisomer gave reduced yields. $(-)_{589}$-$[Co(en)_2(NH_2CH_2CN)Br]Br_2$ was obtained by dissolving the combined diastereoisomer fractions in water (pH 3), passing the solution through Dowex AG-X1 (Br^- form) anion-exchange resin, reducing the eluate to a small volume, and adding NaBr. Anal. Calcd for $CoC_6H_{12}N_6Br_3$: C, 15.17; H, 4.24; N, 17.70. Found: C, 15.4; H, 4.7; N, 17.8. A 0.104% solution in 0.1 M $HClO_4$ gave α_{589} −0.128° and α_{436} 0.279° from which we get $[M]_{584}$ −606° M^{-1} cm^{-1} and $[M]_{436}$ 1320° M^{-1} cm^{-1}. Fractional recrystallization of $(+)_{589}$-$[Co(en)_2(NH_2CH_2CN)Br]Br_2$ obtained from the filtrate gave α_{589} 0.132° and α_{436} −0.261° for a 0.1% solution in 0.1 M $HClO_4$; thus we have $[M]_{589}$ 650° M^{-1} cm^{-1} and $[M]_{436}$ −1290° M^{-1} cm^{-1}. Anal. Found: C, 15.1; H, 4.5; N, 17.4.

cis-$[Co(en)_2Cl(NH_2CH_2CN)]Cl_2$ was prepared in a manner analogous to the preparation of the above bromo complex using *trans*-$[Co(en)_2Cl_2]Cl$. Anal. Calcd for $CoC_6H_{20}N_6Cl_3\cdot 0.5H_2O$: C, 20.56; H, 6.04; N, 23.97. Found: C, 20.8, 20.6; H, 6.1, 5.7; N, 24.0, 23.6; ϵ_{523} 82 in 1 M $NaClO_4$, pH 2. It was resolved by adding sodium (+)-arsenyl tartrate (1.5 g) to a solution of the complex (1.8 g) in dilute HOAc (15 mL, 40 °C, pH 3). Slow cooling and scratching gave the impure $(+)_{589}$ diastereoisomer (2.4 g). This was purified by converting to the chloride salt by tituration with 12.6 M HCl and the chloride salt was reresolved as described above. The resulting diastereoisomer was then recrystallized to constant rotation from warm water (pH 3) and air-dried. Anal. Calcd for $(+)_{589}$-$[CoC_6H_{20}N_6Cl](As_2C_8O_{12}H_4)$: C, 22.46; H, 3.77; N, 11.23. Found: C, 22.4; H, 3.9; N, 11.2. Tituration with NaBr in a little dilute HBr produced the complex bromide salt which was recrystallized from warm (40 °C) dilute HBr by adding NaBr and cooling in an ice bath. It was collected, washed with ethanol, and dried in vacuo. Anal. Calcd for $(+)_{589}$-$CoC_6H_{20}N_6ClBr_2\cdot H_2O$: C, 16.06; H, 4.95; N, 18.74. Found: C, 16.2; H, 5.0; N, 18.7. A 0.11% solution in 10^{-3} M $HClO_4$ gave $[M]_{589}$ +158° M^{-1} cm^{-1} and $[M]_{436}$ −1180° M^{-1} cm^{-1}. Addition of NaBr (1 g) to the filtrate left after the separation of the least soluble diastereoisomer gave the impure $(-)_{589}$ bromide salt, with $[M]_{589}$ −125° M^{-1} cm^{-1} and $[M]_{436}$ +885° M^{-1} cm^{-1}. Recrystallizations as above failed to improve the optical purity of this isomer.

cis-$[Co(en)_2Br(NH_2CH_2CH_2CN)]Br$ was prepared as the aminoacetonitrile complex using *trans*-$[Co(en)_2Br_2]Br$ and aminopropionitrile free base and titrating 1 equiv of diethylamine over 30 min. One recrystallization from hot, dilute HBr gave a pure product. Anal. Calcd for $CoC_9H_{22}N_6Br_3$: C, 17.20; H, 4.54; N, 17.19; Br, 49.02; Co, 12.05. Found: C, 17.1; H, 4.5; N, 16.7; Br, 49.2; Co, 12.5; ϵ_{544} 82 in 0.01 M $HClO_4$.

cis-$[Co(en)_2(OH_2)(NH_2CH_2CN)](NO_3)_2(ClO_4)\cdot H_2O$ was prepared by treating *cis*-$[Co(en)_2Br(NH_2CH_2CN)](ClO_4)_2$ (2.0 g, 4 mmol) with hypochlorous acid (100 mL). The HOCl solution was prepared by saturating a 0.1 M $AgNO_3$ solution with chlorine at 0 °C with constant swirling to coagulate the precipitated AgCl. Excess dissolved chlorine was back-titrated with 1.0 M $AgNO_3$ solution until no new precipitate was formed, AgCl was removed by filtration through filter paper pulp, and the filtrate was immediately used at 0 °C. The purple solution rapidly turned red. After ca. 5 min precipitated AgBr was removed and the solution quickly concentrated to ca. 20 mL on a vacuum evaporator. Addition of excess $LiNO_3$ and $NaClO_4$ and cooling in an ice bath caused orange *cis*-$[Co(en)_2(OH_2)(NH_2CH_2CN)](NO_3)_2(ClO_4)$ to crystallize. This material was twice recrystallized from the minimum volume of cold 0.1 M $HClO_4$ by addition of $LiNO_3$ and $NaClO_4$ and cooling (yield 1.7 g). Anal. Calcd for $CoC_6H_{22}O_{11}N_8Cl\cdot H_2O$: C, 14.57; H, 4.89; N, 22.65; Co, 11.91; Cl, 7.17. Found: C, 14.7; H, 5.0; N, 22.8; Co, 11.9; Cl, 7.2; ϵ_{488} 83 and ϵ_{352} 78 in 0.01 M $HClO_4$–1 M $NaClO_4$. Oxygen-18-labeled *cis*-$[Co(en)_2(^{18}OH_2)(NH_2CH_2CN)](NO_3)_2(ClO_4)$ was similarly prepared using 1.2 g of the bromo complex and ca. 20 mL of the HOCl solution prepared using 1.5 atom % $H_2{}^{18}O$. Attempts to prepare the aqua complex by removing coordinated Br^- with Pb^{2+}, Ag^+, or Tl^{3+} were unsuccessful.

cis-$[Co(en)_2(OH_2)(NH_2CH_2CH_2CN)](NO_3)_2(ClO_4)$ was prepared by dropwise addition of 0.43 M $Hg(ClO_4)_2$ (17.5 mL) in 1.3 M $HClO_4$ to *cis*-$[Co(en)_2Br(NH_2CH_2CH_2CN)]Br_2$ (2.45 g, 5 mmol) dissolved in water (90 mL) containing 10 drops of concentrated $HClO_4$. After being stirred for 10 min, the red solution was concentrated to ca. 30 mL, precipitated $HgBr_2$ was removed, and excess $LiNO_3$ and $NaClO_4$ were added. On cooling of the mixture, the orange $[Co(en)_2(OH_2)(NH_2CH_2CH_2CN)](NO_3)_2(ClO_4)$ crystallized. This material was filtered off, washed with ethanol, air-dried, and then recrystallized from the minimum volume of 0.1 M $HClO_4$ by addition of $LiNO_3$ and $NaClO_4$ and cooling (yield 1.9 g). Anal. Calcd for $CoC_7H_{24}O_{11}N_8Cl$: C, 17.13; H, 4.93; N, 22.84; Cl, 7.22; Co, 12.01. Found: C, 17.1; H, 4.8; N, 22.1; Cl, 7.2; Co, 12.1; ϵ_{486} 80 and ϵ_{351} 74 in 0.01 M $HClO_4$–1 M $NaClO_4$.

The monodentate β-alanine amide complex *cis*-$[Co(en)_2Br(\beta\text{-}alaNH_2)]Br_2\cdot H_2O$ was prepared by a method essentially that described by Baraniak.[19] Anal. Calcd for $CoC_7H_{24}N_6OBr_3\cdot H_2O$: C, 16.01; H, 4.99; N, 16.00. Found: C, 16.1; H, 5.0; N, 16.1; ϵ_{540} 101 in 10^{-3} M $HClO_4$. The β-alanine amide chelate complex $[Co(en)_2(\beta\text{-}alaNH_2)](ClO_4)_3$ was also prepared as described by Baraniak.[19] Anal. Calcd for $CoC_7H_{24}N_6O_{12}Cl_3$: C, 14.86; H, 4.28; N, 14.86. Found: C, 14.58; H, 4.38; N, 14.50; ϵ_{493} 116 and ϵ_{350} 93.5 in H_2O.

Chelation of *cis*-$[Co(en)_2(^{18}OH_2)(NH_2CH_2CN)]ClO_4(NO_3)_2$. The complex (0.4 g) in a solution of 0.02 M $Hg(ClO_4)_2$–0.01 M $HClO_4$ (10 mL) was kept for 10 min at 25 °C and then the solution was reduced to a small volume under reduced pressure. On addition of $LiNO_3$ and $NaClO_4$, red crystals of the chelated amide complex $[Co(en)_2glyNH_2]ClO_4(NO_3)_2$ were obtained (0.25 g). This complex, after drying, was heated to 250 °C in a MS902 mass spectrometer. Glycine amide distilled in preference to other ligands. The ^{18}O content was measured by comparing the mass 76:mass 74 ratio with that obtained from the unenriched complex. Several determinations were made.

Reaction Products. Following kinetic runs, representative solutions were acidified to pH ~4 and adsorbed and eluted ($NaClO_4$ or HCl) from Dowex 50W-X2 ion-exchange resin. For the Hg^{2+}-catalyzed reactions with *cis*-$[Co(en)_2Cl(NH_2CH_2CN)]Cl_2$ and *cis*-$[Co(en)_2Br(NH_2CH_2CN)]Br_2$ small amounts of a 2+ band ($NaClO_4$ eluent) were observed and many experiments (Table III) were carried out on larger amounts of material. The complex (1.5 g) was dissolved in the $Hg(ClO_4)_2$ solution; the mixture was left overnight at 25.0 °C, diluted, adsorbed on Dowex 50W-X2 resin, and washed with a little water. The minor 2+ product was eluted with 1 M $NaClO_4$ and the major 3+ band with 2–3 M HCl. The fractions were estimated by spectrophotometry at 479 and 487 nm, respectively, and by atomic absorption for Co. The major products from several experiments were combined and reduced to dryness by vacuum evaporation at ~50 °C; the dry residue was washed on a filter with ethanol and acetone. It was crystallized as orange $[Co(en)_2(glyNH_2)](NO_3)_2(ClO_4)\cdot 2H_2O$ from the minimum volume of warm water by adding $LiNO_3$ and $NaClO_4$ and cooling. Anal. Calcd for $[CoC_6H_{22}N_8O_{11}Cl]\cdot 2H_2O$: C, 14.05; H, 5.11; N, 21.86. Found: C, 14.1; H, 5.1; N, 21.7. The minor product was isolated from a large-scale experiment. To *cis*-$[Co(en)_2Br(NH_2CH_2CN)](ClO_4)_2$ (20.4 g) dissolved in 0.1 M $HClO_4$ (340 mL) was added, with stirring, 60 mL of 1 M $Hg(ClO_4)_2$ which was 0.1 M in $HClO_4$. After 15 min the red solution was diluted to 5 L, adsorbed on Dowex 50W-X2 resin, washed with water, and eluted with 1 M $NaClO_4$ (pH 3) until the two orange-red bands were well separated. The eluent was then changed to 1 M HCl, and the first minor band, which had turned yellow, was collected. The solution was concentrated to ~300 mL, HCl removed by passing through a Dowex AG3-X4 (200–400 mesh) column (basic form), and the eluate reduced to dryness. The orange powder was dissolved in a small volume of water, the mixture was filtered, and $LiNO_3$ was added. Addition of ethanol and cooling resulted in the slow formation of orange crystals which were dried in vacuo. Anal. Calcd for $[Co(C_6H_{21}N_6O)](NO_3)_2$:

C, 19.16; H, 5.63; N, 29.78. Found: C, 19.4; H, 4.9; N, 29.4. The ^{1}H NMR spectrum was run in D_2O–D_2SO_4 and the visible spectrum recorded in 2 M HCl and at pH 0.74, 1.40, 2.57, and 11.7. For ^{1}H NMR spectra in Me_2SO-d_6 the perchlorate salt was prepared using Dowex AG1 (ClO_4^-) ion-exchange resin.

The ^{1}H NMR spectra of the products of the Hg^{2+}-catalyzed reactions were also determined. The bromo complex (60 mg) was mixed with 0.4 mL of 1 M $HgClO_4$ in D_2O–$DClO_4$ (0.1 M). The insoluble mercury salts were removed by filtration and the ^{1}H NMR spectrum (HA-100) was run within 5 min of mixing. The solution was left overnight and rescanned; no significant changes were observed. For comparison, a spectrum of authentic $[Co(en)_2(glyNH_2)](NO_3)_2ClO_4$ in the same solution was recorded.

The products of the Hg^{2+}-catalyzed and the uncatalyzed hydrolyses of $[Co(en)_2(OH_2)(NH_2CH_2CN)](NO_3)_2(ClO_4)$ were determined by spectrophotometry (280–600 nm), by ion-exchanging the product solutions on Dowex 50W-X2 or Sephadex CM-25 resins ($NaClO_4$ eluent, pH ~8), by isolation of the major products as crystalline solids, and by ^{1}H NMR spectra. For the uncatalyzed hydrolysis of $[Co(en)_2(OH_2)(NH_2CH_2CN)](NO_3)_2(ClO_4)$ the solutions from several kinetic runs were combined and chromatographed on Dowex 50W-X2 ($NaClO_4$ (pH 8), then 2–3 M HCl), and the product was isolated as the mixed nitrate–perchlorate salt. Anal. Found for $[Co(en)_2(glyNH_2)](NO_3)_2ClO_4{\cdot}2H_2O$: C, 13.9; H, 5.3; N, 21.9. Similarly, with the Hg^{2+}-catalyzed hydrolysis of the aqua–propionitrile complex, $[Co(en)_2(\beta\text{-alaNH}_2)](ClO_4)_3$ was isolated following ion-exchange chromatography (3 M HCl) and recrystallized from hot water. Anal. Found: C, 14.7; H, 4.4; N, 14.9.

pK_a Determinations. For *cis*-$[Co(en)_2(OH_2)(NH_2CH_2CN)](NO_3)_2(ClO_4)$ aliquots of a stock 0.01 M solution of the complex in 0.02 M $HClO_4$ (200 mL) were rapidly mixed in a manually operated stopped-flow device with equal volumes of 0.2 M acetate or imidazole buffer solutions (1 M $NaClO_4$). The initial OD on mixing (~1 s) was measured at 488, 498, and 510 nm on the Cary 16 K spectrophotometer, and the final pH was recorded. Measurements covered the pH range 3.9–7.5, and the pK_a evaluated from the OD changes observed at the three wavelengths was 5.60 ± 0.05 (25.0 °C, μ = 1.0 M ($NaClO_4$)).

For *cis*-$[Co(en)_2(OH_2)(NH_2CH_2CH_2CN)](NO_3)_2ClO_4$ hydrolysis of the nitrile group is insignificant between pH 2 and 9 over long periods (several hours). A 0.01 M solution (~25 mL) in 1 M $NaClO_4$ was titrated with a concentrated NaOH solution and back-titrated with ca. 10 M $HClO_4$. The spectrum was recorded (300–600 nm) at 12 pHs between 1.92 and 8.35 and the pK_a evaluated at 500 and 390 nm. Both wavelengths gave pK_a = 5.72 ± 0.03 (25.0 °C, μ = 1.0 ($NaClO_4$)). Isosbestic points occurred at 429 and 467 nm.

Thin-Layer Chromatography. For the free ligands, the compound was dissolved in HCl (0.1 M) and a small drop was applied to the silica gel plate and dried. The plate was eluted with 1-butanol, HCl (12 M), and H_2O (8:1:1) and developed with ninhydrin spray at 80 °C for ~15 min. For the cobalt complexes, the ligand was released in a HCl (0.1 M) solution using a slight excess of $NaBH_4$ to reduce the cobalt to Co(II). The solution was then treated as above. Blank experiments on the free ligands in the presence of Hg^{2+} were also run in conjunction with the reaction solutions. Reactions of complexes with Hg^{2+} were allowed to proceed ~2 min before addition of $NaBH_4$. For the aminoacetonitrile and glycine amide ligands and complexes the nitrile eluted as a separate spot (yellow test) but ethylenediamine (violet test) and glycine amide (blue test) moved together. For the aminopropionitrile and β-alanine amide complexes or free ligands, the nitrile, ethylenediamine, and β-alaNH_2 all clearly separated.

Kinetic Data. Intramolecular hydration of the coordinated nitrile group and the Hg^{2+}-promoted removal of Br^- were followed spectrophotometrically using Gilford 2400 or Cary 14, 16K, or 118C spectrophotometers at 25.0 ± 0.1 °C and μ = 1.0 M ($NaClO_4$). For the faster reactions a manually driven stopped-flow mixing device was fitted, and, on occasions ($k_{obsd} > 0.4\ s^{-1}$), a Durrum-Gibson D-108 stopped-flow spectrophotometer was used. Some kinetic data were obtained polarimetrically using a Perkin-Elmer P22 spectropolarimeter (thermostated 1-dm cell) fitted with the mixing device. Buffers used to control pH were HOAc–NaOAc (0.2 M) and imidazole–$HClO_4$ (0.2 M), and corrections for buffer effects were made (when necessary) by extrapolation of the first-order rate constants to zero buffer concentration. The solution pH was routinely measured before, during, and after the reaction and experiments were rejected when this changed by more than 0.01 unit. Reactions were followed for at least 6 half-lives, and first-order rate constants were obtained using infinity, and occasionally Guggenheim, plots. These plots were linear for at least 3 half-lives.

The following details relate to specific experiments.

(a) The Hg^{2+}-induced removal of Br^- from *cis*-$[Co(en)_2Br(NH_2CH_2CN)]Br_2$ was carried out by mixing a stock ~6 mM solution of the complex in 0.10 M $HClO_4$ with an equal volume of the Hg^{2+} solution, 2.1 M in $NaClO_4$. The Hg^{2+} solution was prepared by dissolving HgO in 2.08 M $HClO_4$. For the polarimetric data $(-)_{589}$-*cis*-$[Co(en)_2Br(NH_2CH_2CN)]Br_2{\cdot}H_2O$ (1.4 mM) was used.

(b) The Hg^{2+}-induced formation of $[Co(en)_2(glyNH_2)]^{3+}$ from $[Co(en)_2(OH_2)(NH_2CH_2CN)](NO_3)_2ClO_4$ was carried out using 5–10 mM solutions of the aqua complex made up in 0.10, 0.50, or 0.01 M $HClO_4$ and adding the Hg^{2+} solution (1 M–1 mM) made up in 0.1 or 0.5 M $HClO_4$ and containing added $NaClO_4$ sufficient to make the final combined ionic strength 1.0 or 3.5 M. For the Ag^+-, Zn^{2+}-, and Cd^{2+}-catalyzed reactions, the metal nitrate salts were used.

(c) The Hg^{2+}-catalyzed formation of $[Co(en)_2(\beta\text{-alaNH}_2)]^{3+}$ from the isolated aquapropionitrile complex was initiated in a similar manner to (a) above and was followed by repetitive scans at 300–600 nm on the Cary 118C spectrophotometer and at 486 nm on the Gilford 2400 spectrophotometer (0.5 OD slide-wire). Some runs were carried out using as starting complex *cis*-$[Co(en)_2Br(NH_2CH_2CH_2CN)]Br_2$. A solution of the complex (18 mM) was made up to the desired $HClO_4$ concentration, μ = 1.0 ($NaClO_4$), mixed by hand with the $Hg(ClO_4)_2$ solution (0.08–0.20 M), and transferred to a thermostated 1-cm cell in the Gilford 2400 spectrophotometer. Under these conditions the rapid removal of Br was not observed.

(d) The uncatalyzed intramolecular hydrolysis in *cis*-$[Co(en)_2(OH)(NH_2CH_2CN)]^{2+}$ was followed by mixing a freshly prepared solution of *cis*-$[Co(en)_2(OH_2)(NH_2CH_2CN)](NO_3)_2(ClO_4)$ (2–10 mM) in 1 M $NaClO_4$ with an equal volume of 0.2 M buffer made up to 1 M ($NaClO_4$) and following the OD change in the region 488–474 nm using a 0.1 OD slide-wire. Reactions were first order in the Co(III) complex.

(e) Attempts to observe hydrolysis in the $[Co(en)_2(OH)(NH_2CH_2CH_2CN)]^{2+}$ were made by mixing a 5 mM solution of the aqua complex (1 M $NaClO_4$) with an equal volume of 0.2 M buffer (1 M $NaClO_4$). Solutions were made up at pH 7.63, 7.00, and 6.57 (imidazole) and 5.93, 5.58, and 4.90 (acetate) and thermostated at 25.0 °C. Optical densities were measured at irregular time intervals. No spectral change was observed over 832 h (25 °C) at the three higher pHs; for the other runs (acetate buffers) a very slow and small OD increase was observed at 490 nm consistent with formation of the chelated β-alaninate complex (ϵ_{493} 126, ϵ_{350} 93). Similarly, no nitrile hydrolysis was observed at 50 °C at pH 6.81 and 7.15 (1 M $NaClO_4$) and a slow collapse of the absorption spectrum occurred over 5 days indicating some decomposition of the complex.

Results

Hg^{2+}-Catalyzed Reactions of *cis*-$[Co(en)_2(NH_2CH_2CN)X]^{2+}$ (X = Br, Cl). Treatment of an aqueous acidic solution of *cis*-$[Co(en)_2(NH_2CH_2CN)Br](ClO_4)_2$ with Hg^{2+} results in a rapid color change from purple to red-orange. Only one reaction was observed spectrophotometrically (300–600 nm) and spectropolarimetrically (465 nm), and the rate data given in Table I fit the rate law $k_{obsd} = k_{Hg}[Hg^{2+}]$ over the concentration range 0.5 M–2.5 mM Hg^{2+}. The reaction rate is $[H^+]$ independent from 0.9 to 0.09 M and the second-order rate constant, $k_{Hg} = 0.12 \pm 0.2\ M^{-1}\ s^{-1}$ (25 °C, μ = 1.0 M ($NaClO_4$)), has a significantly smaller value than those found for related *cis*-$[Co(en)_2(amine)Br]^{2+}$ complexes, Table II. The latter values were obtained from data collected under conditions identical with those for the nitrile complex, and the same rate law as the above was followed in each case. For $[Co(en)_2(NH_2CH_2CN)Cl]^{2+}$ $k_{Hg} = 8.4 \times 10^{-4}\ M^{-1}\ s^{-1}$ at μ = 2.0 M ($NaClO_4$).

Ion-exchange chromatography of the reaction products showed the presence of two orange-red ions, the major species (~93%) eluting as a 3+ ion on Dowex 50W-X2 cation-exchange resin and the minor component (~7%) as a 2+ ion. Both ions were isolated as crystalline solids and characterized by elemental analysis, ^{1}H NMR spectra (Figure 1), and visible spectra (Figure 2). The major 3+ product was shown to be

Table I. Rate Data for the Hg^{2+}-Catalyzed Reaction of *cis*-$[Co(en)_2Br(NH_2CH_2CN)](ClO_4)_2$ at 25.0 °C[a]

$[Hg^{2+}]$, M	[Co(III)], M	$[H^+]$, M	10^2k_{obsd}, s^{-1}	10^2k_{Hg},[e] M^{-1} s^{-1}
0.50[b]	3×10^{-3}	0.09	7.40	15
0.20[b]	3×10^{-3}	0.09	2.57	13
0.10[b]	3×10^{-3}	0.09	1.39	14
0.10[b]	3×10^{-3}	0.89	1.42	14
0.10[b]	5×10^{-4}	0.10	1.09	11
0.05[b]	5×10^{-4}	0.10	0.55	11
0.0025[b]	4×10^{-4}	0.10	0.031	12
0.50[c]	7×10^{-4}	0.09	6.9	14
0.38[c]	7×10^{-4}	0.09	4.7	12
0.38[c]	7×10^{-4}	0.83	4.8	13
0.50[d]	5×10^{-4}	0.25	0.037	0.084

[a] $\mu = 1.05$ M ($NaClO_4$) except for $[Hg^{2+}] = 0.5$ M (no added $NaClO_4$). [b] Spectrophotometric data at 560 nm. [c] Polarimetric data at 465 nm. [d] Data for *cis*-$[Co(en)_2Cl(NH_2CH_2CN)]Cl_2$; $\mu = 2.0$ M ($NaClO_4$). [e] $k_{Hg} = k_{obsd}/[Hg^{2+}]$.

Table II. Second-Order Rate Constants for the Hg^{2+}-Catalyzed Aquations of *cis*-$[Co(en)_2Br(amine)](ClO_4)_2$ Complexes (25.0 °C, $\mu = 1.0$ M ($NaClO_4$))

Amine	pK_a(amine)	k_{Hg},[b] M^{-1} s^{-1}
NH_3	9.2	2.7
NH_2CH_3	10.66	7.9
$NH_2CH_2CO_2CH_3$	7.59	5.1
$NH_2CH_2CO_2C_2H_5$	7.64	4.4
$NH_2CH_2CH_2CO_2C_3H_6$	9.43	2.4
$NH_2CH_2CH_2CO_2H$	10.24[a]	2.9
$NH_2CH_2CO_2C_3H_7$	7.68	5.1
NH_2CH_2CN	5.34	0.12

[a] pK_a for dipolar form. [b] $k_{Hg} = k_{obsd}/[Hg^{2+}]$.

$[Co(en)_2(glyNH_2)]^{3+}$ containing the N–O chelated glycine amide by comparing it with authentic $[Co(en)_2(glyNH_2)](NO_3)_2ClO_4$ prepared separately from $[Co(en)_2(glyNH_2)Br](ClO_4)_2$.[21] It could not be rebrominated by heating with HBr. Also, treatment of $(+)_{589}$-$[Co(en)_2(NH_2CH_2CN)Br]Br_2$ ($[M]_{589}$ +651° M^{-1} cm^{-1}, $[M]_{436}$ −1287° M^{-1} cm^{-1}) with $Hg(ClO_4)_2$ (0.1 M, 0.05 M in $HClO_4$) gave after 10 min a rotatory dispersion curve (ORD) essentially that of $(+)_{589}$-$[Co(en)_2(glyNH_2)]^{3+}$ ($[M]_{589}$ 1440° M^{-1} cm^{-1}, $[M]_{465}$ −4660° M^{-1} cm^{-1} 85% active). The rotatory dispersion curves of $(+)_{589}$-$[Co(en)_2(NH_2CH_2CN)(OH_2)]^{3+}$ (Figure 3) and $(+)_{589}$-$[Co(en)_2(glyNH_2)(OH_2)]^{3+}$ [23] are significantly different having much lower molecular rotations from 600 to 300 nm.

A similar result was obtained with $(+)_{589}$-$[Co(en)_2(NH_2CH_2CN)Cl]Br_2 \cdot H_2O$ although in this case 98% optically pure $(+)_{589}$-$[Co(en)_2(glyNH_2)]^{2+}$ was realized.

The absence of nitrile following treatment with Hg^{2+} was verified by thin-layer chromatography. Whereas reduction of $[Co(en)_2(NH_2CH_2CN)Br]Br_2$ with $NaBH_4$ gave a positive yellow spot for the nitrile, similar treatment following reaction with Hg^{2+} gave no nitrile but a positive test (violet) for glycine amide together with ethylenediamine.

Analytical data for the isolated minor product fit the composition $[Co(en)_2(NH_2CH_2CONH)](NO_3)_2$ and the absence of aminoacetonitrile was verified by thin-layer chromatography following reduction with $NaBH_4$. The magnitude of the optical rotations for the product produced from $(+)_{589}$-$[Co(en)_2(NH_2CH_2CN)Br]Br_2$ ($[M]_{546}$ ~2500° M^{-1} cm^{-1}) suggest the presence of a chelated moiety, and its other properties were similar to those reported for the N–N chelated glycine amide complex $[Co(NH_3)_4(NH_2CH_2CONH)](ClO_4)_2$.[24] Thus, under acidic conditions ($HClO_4$ or HCl, pH ≤1) it eluted from the ion-exchange resin as a yellow 3+ ion but with $NaClO_4$ (pH ≥4) it moved more rapidly as a red-orange 2+ ion. Also, 1 equiv of acid was consumed between pH 3 and 0.7, and spectrophotometric titration at 390 and 520 nm gave a pK_a of 1.2 ± 0.1 for the acidic group. Addition of H_2SO_4 to a Me_2SO-d_6 solution of the complex in the ¹H NMR tube (orange to yellow color change) results in the low-field shift of the glycine CH_2 resonance and the appearance of a sharp singlet integrating for 1 H; this resonance moves to lower field as H_2SO_4 is added, Figure 4. A similar situation was found with $[Co(NH_3)_4(NH_2CH_2CONH)]^{2+}$ [24] and was attributed to changes in the chemical shift of the amide NH proton as the carbonyl function became protonated. (See eq 1.)

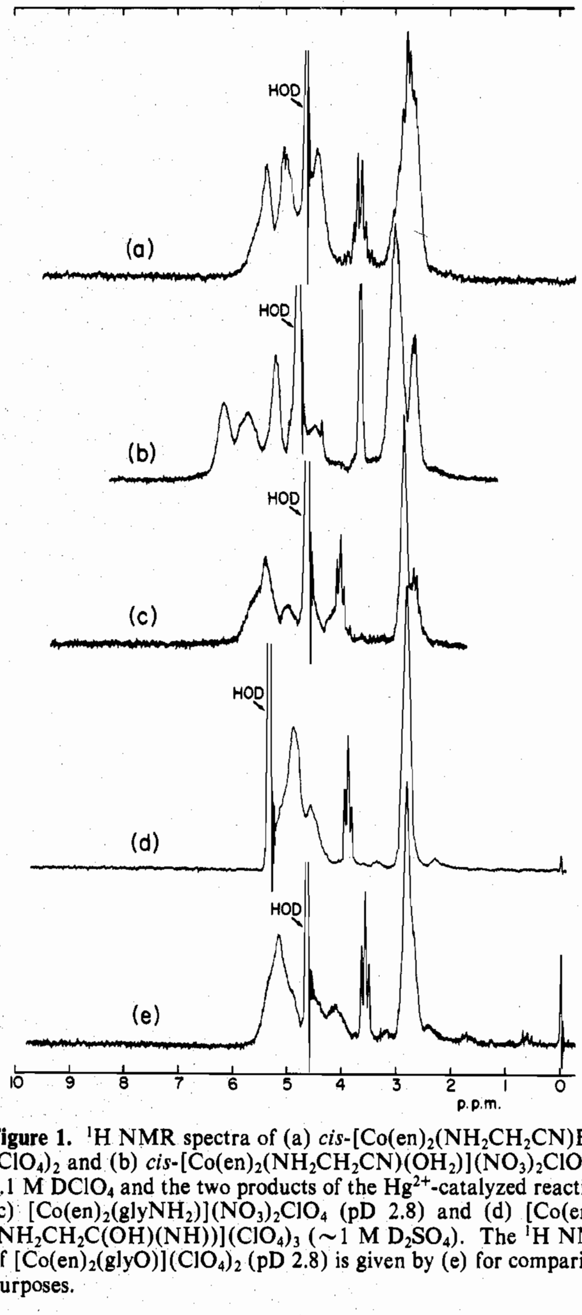
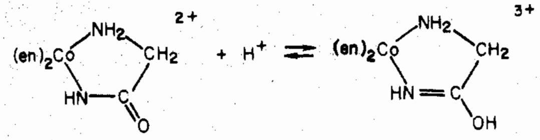


Figure 1. ¹H NMR spectra of (a) *cis*-$[Co(en)_2(NH_2CH_2CN)Br](ClO_4)_2$ and (b) *cis*-$[Co(en)_2(NH_2CH_2CN)(OH_2)](NO_3)_2ClO_4$ in 0.1 M $DClO_4$ and the two products of the Hg^{2+}-catalyzed reaction, (c) $[Co(en)_2(glyNH_2)](NO_3)_2ClO_4$ (pD 2.8) and (d) $[Co(en)_2(NH_2CH_2C(OH)(NH))](ClO_4)_3$ (~1 M D_2SO_4). The ¹H NMR of $[Co(en)_2(glyO)](ClO_4)_2$ (pD 2.8) is given by (e) for comparison purposes.



(1)

The distributions of products for *cis*-$[Co(en)_2(NH_2CH_2CN)Br]^{2+}$ and *cis*-$[Co(en)_2(NH_2CH_2CN)Cl]^{2+}$ under various conditions are given in Table III. The results

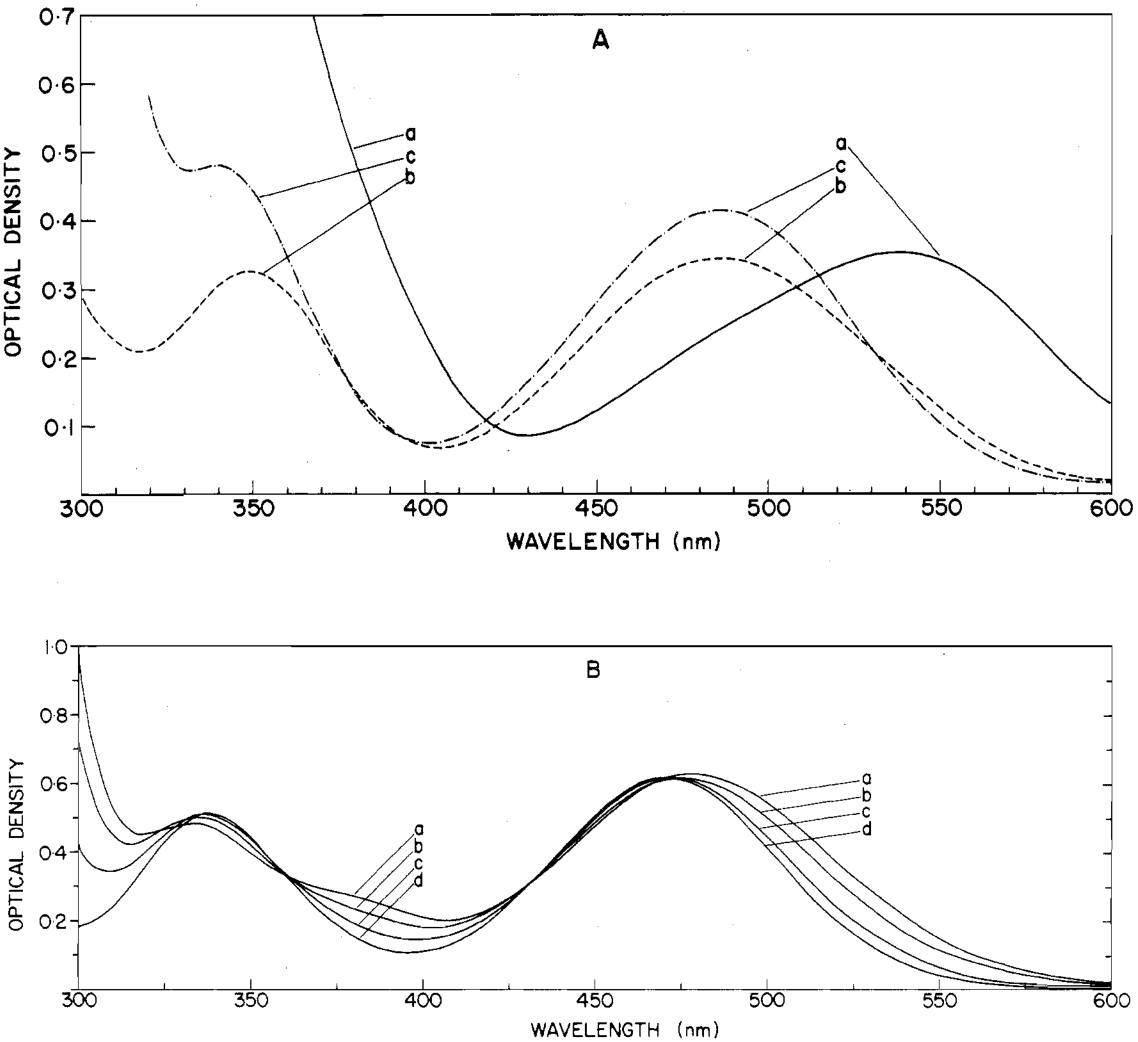
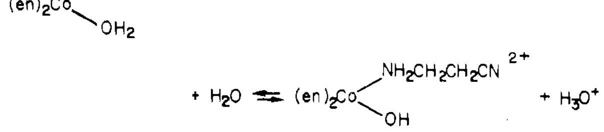


Figure 2. (A) Visible spectra: (a) *cis*-$[Co(en)_2(NH_2CH_2CN)Br]Br_2$, — ($\epsilon_{542}$ 84); (b) *cis*-$[Co(en)_2(NH_2CH_2CN)(OH_2)](NO_3)_2ClO_4$, - - - ($\epsilon_{484}$ 80); (c) $[Co(en)_2(glyNH_2)](NO_3)_2ClO_4$, –•–•, isolated from reaction of either (a) or (b) with Hg^{2+} (2.2×10^{-3} M solutions, 20-mm path length, 0.1 M $HClO_4$). (B) Titration of 2.5×10^{-3} M aqueous solution of $[Co(en)_2(NH_2CH_2CONH)](NO_3)_2$ with HCl (20-mm path length): (a) pH 2.57 (ϵ_{479} 133); (b) pH 1.40; (c) pH 0.74; (d) 2 M HCl (ϵ_{471} 124).

show that the amount of the minor N–N bound amide (2+) is independent of $[Hg^{2+}]$, $[H^+]$, time of reaction, source of the aminoacetonitrile ligand (locally prepared or purchased), and possibly the ionic strength ($NaClO_4$). Also, fractional recrystallization of the complexes, changing the accompanying anion (Cl, ClO_4; Br, ClO_4), and ion-exchange fractionation did not alter the product analysis results. The table also shows that the bromo complex gives statistically more of the N–N bound amide (6.9 ± 1.0%) than does the chloro complex (4.0 ± 0.2%).

Hg^{2+}-Catalyzed Reaction of *cis*-$[Co(en)_2(NH_2CH_2CH_2CN)Br]^{2+}$. The immediate product following removal of bromide ion is the aqua ion $[Co(en)_2(NH_2CH_2CH_2CN)(OH_2)]^{3+}$. The continuing presence of nitrile was demonstrated by thin-layer chromatography (pale brown spot) following reduction with $NaBH_4$, and the complex was isolated and characterized as $[Co(en)_2(NH_2CH_2CH_2CN)(OH_2)](NO_3)_2ClO_4$ (infrared: strong absorption 2250 cm^{-1} (nitrile); no strong absorption at 1680–1640 cm^{-1} (amide)). Ion exchange of the final solution using both 1 M $NaClO_4$ (pH 4) and 1 M $HClO_4$ resulted in a single 3+ band, and the product spectrum (ϵ_{488}(max) 80, ϵ_{354}(max) 73 in 0.5 M Hg^{2+}, 0.1 M $HClO_4$) was identical with that for the isolated complex and considerably different from that for $[Co(en)_2(\beta\text{-alaNH}_2)]^{2+}$. No 2+ species corresponding to the glycine imide product produced in the $[Co(en)_2(NH_2CH_2CN)Br]^{2+} + Hg^{2+}$ reaction was observed. The product solution could also be rebrominated by heating in aqueous HBr solution and the $[Co(en)_2(NH_2CH_2CH_2CN)Br]^{2+}$ produced was characterized by ion-exchange chromatography.

Titration data gave pK_a = 5.72 ± 0.03 for the aqua complex at 25 °C, μ = 1.0 M ($NaClO_4$). (See eq 2.) The red-violet



$$[(en)_2Co(NH_2CH_2CN_2CN)(OH_2)]^{3+} + H_2O \rightleftharpoons [(en)_2Co(NH_2CH_2CH_2CN)(OH)]^{2+} + H_3O^+ \quad (2)$$

hydroxo ion has a characteristic absorption spectrum (Figure 2) and moves as a 2+ ion on the ion-exchange resin. The same aqua species could also be produced by treatment of $[Co(en)_2(NH_2CH_2CH_2CN)Br]Br_2$ with HOCl.

Prolonged treatment of the $[Co(en)_2(NH_2CH_2CH_2CN)Br]^{2+}$ ion with Hg^{2+} gave the chelated β-alanine amide complex ion $[Co(en)_2(\beta\text{-alaNH}_2)]^{3+}$. Thus after several days in the presence of Hg^{2+}, no aqua or chelated β-alanine imide species, $[Co(en)_2(NH_2CH_2CH_2CONH)]^{2+}$, could be detected by ion-exchange chromatography (pH ~8, $NaClO_4$). The presence of β-alanine amide in the product solution was

Table III. Reaction Products for the Hg^{2+}-Catalyzed Reactions of $[Co(en)_2X(NH_2CH_2CN)]X_2$ (X = Cl, Br)[a]

Prepn[b]	$[Hg(ClO_4)_2]$, M	$[HClO_4]$, M	$[NaClO_4]$, M	Vol, mL	Products[g] 2+	Products[g] 3+
			$[Co(en)_2Br(NH_2CH_2CN)]Br_2$			
1	0.2	0.09	0	100	8.5 (s)	91.5 (s)
1	0.2	0.09	0.3	75	6.1 (s), 7.2 (a)	93.9 (s), 92.8 (a)
2	0.1	0.09	1.6	100	7.3 (s)	92.7 (s)
2	0.2	0.09	1.3	50	7.6 (s)	92.4 (s)
2	0.5	0.22	0.5	25	8.2 (s)	91.8 (s)
2	0.5	0.22	1.0	25	7.9 (s)	92.1 (s)
3[c]	0.2	0.09	1.3	75	6.6 (s)	93.4 (s)
4	0.2	0.09	1.3	75	5.4 (s)	94.6 (s)
4[d]	0.2	0.09	1.3	50	6.2 (s)	93.8 (s)
5	0.2	0.09	0	200	5.6 (s), 6.6 (a)	94.4 (s), 93.4 (a)
5	0.5	0.25	2.0		6.6 (s), 7.4 (a)	93.4 (s), 92.6 (a)
			$[Co(en)_2Cl(NH_2CH_2CN)]Cl_2$			
1[e]	0.5	0.05	0.5	50	3.5 (s)	96.5 (s)
1	0.2	0.09	0	100	3.6 (s)	96.4 (s)
1[f]	0.2	0.09	0.3	100	4.0 (s)	96.0 (s)
2	0.02	0.09	0	100	4.0 (s), 5.0 (a)	96.0 (s), 95.0 (a)
2	0.2	0.09	0	200	4.5 (s), 5.0 (a)	95.5 (s), 95.0 (a)
2[d]	0.2	0.09	0	100	4.9 (s), 5.7 (a)	95.1 (s), 94.3 (a)
2[d]	0.2	0.09	0	200	4.2 (s), 5.8 (a)	95.8 (s), 94.2 (a)
3	0.5	0.25	2.0		4.2 (s), 5.2 (a)	95.8 (s), 94.8 (a)

[a] One gram of complex was used in each experiment; products were determined after 8–12 h at 25.0 °C. [b] This column indicates different preparations of the complex. [c] ClO_4^- salt of complex. [d] Third fraction of recrystallized 4 (bromo complex) or 2 (chloro complex). [e] Reaction time 2 h. [f] Reaction time 5 h. [g] Isolated fractions were analyzed either by spectrophotometry (s) or by atomic absorption (a). Generally >98% recoveries were obtained and the results are adjusted to 100%.

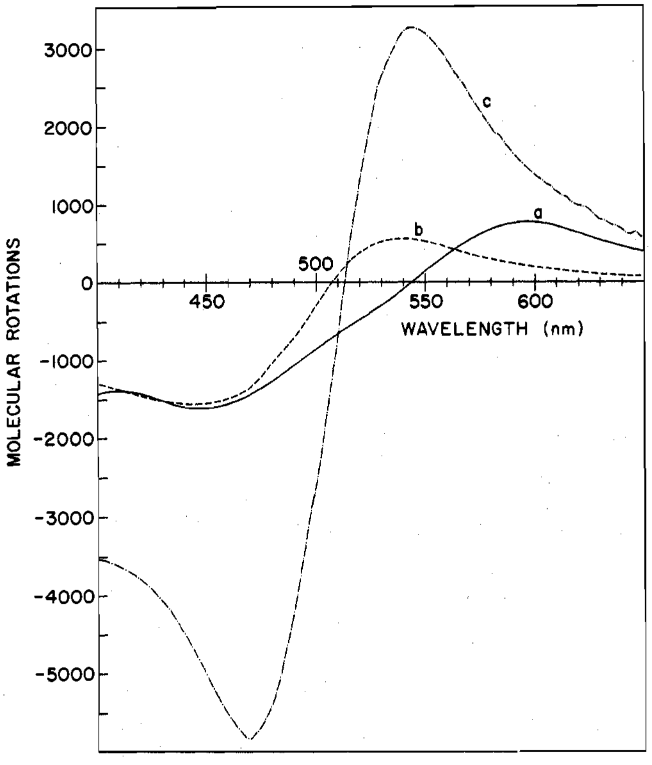


Figure 3. Rotatory dispersion curves: (a) $(+)_{489}$-$[Co(en)_2(NH_2CH_2CN)Br]Br_2$, —; (b) $(+)_{589}$-$[Co(en)_2(NH_2CH_2CN)(OH_2)](NO_3)_2ClO_4$, - - -; (c) $(+)_{589}$-$[Co(en)_2(glyNH_2)]^{3+}$, – · – ·, produced by reacting (b) with 0.1 M Hg^{2+} (all in 0.1 M $HClO_4$).

demonstrated by thin-layer chromatography; when analysis was carried out immediately after reaction with Hg^{2+} (loss of purple color) only nitrile (pale brown) and ethylenediamine (violet) were detected. However, after the solution was allowed to stand for several days, analysis showed only amide (pale blue) and ethylenediamine (violet). The visible spectrum of the final solution (ϵ_{493}(max) 123, ϵ_{351}(max) 86 in 0.1 M $HClO_4$, 0.1 M Hg^{2+}) was identical with that of authentic

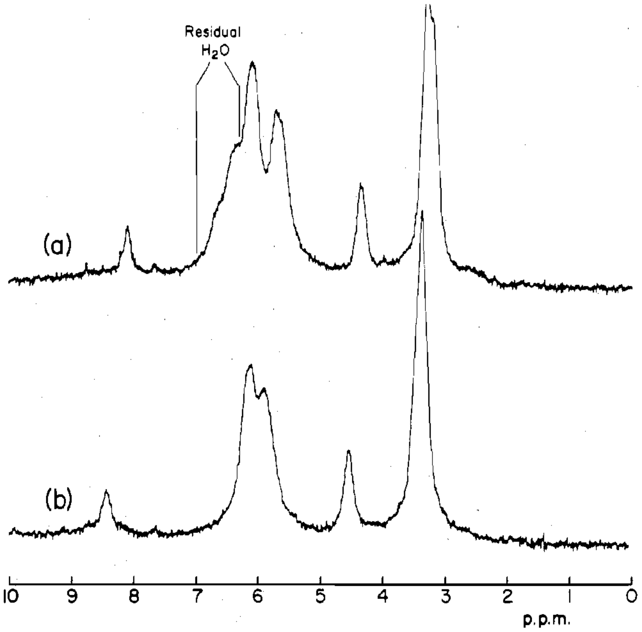
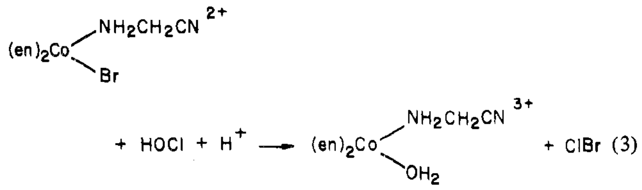


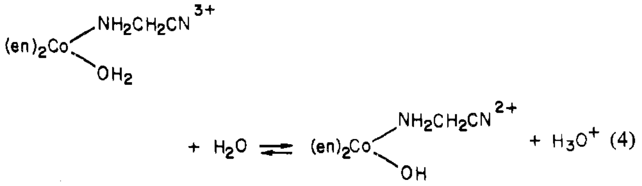
Figure 4. ^1H NMR spectra of $[Co(en)_2(NH_2CH_2CONH)](ClO_4)_2$ in (a) Me_2SO-d_6 and (b) Me_2SO-d_6 containing 1 drop of concentrated H_2SO_4. The signal at lowest field (~8 ppm) is attributed to the single –NH– resonance and moves to lower frequency (~8.5 ppm) on protonation of the >C═O function; the –CH_2– resonance (4.3 ppm) also moves to lower field (4.5 ppm).

$[Co(en)_2(\beta\text{-alaNH}_2)](ClO_4)_3$ prepared separately from $[Co(en)_2(\beta\text{-alaNH}_2)Br]Br_2$, and attempts to rebrominate the product solution using HBr failed. Also, $[Co(en)_2(\beta\text{-alaNH}_2)](ClO_4)_3$ was isolated and characterized by elemental analysis. It is clear that this species is formed subsequent to the aqua ion, and details of this reaction will be dealt with below.

The *cis*-$[Co(en)_2(NH_2CH_2CN)(OH_2)]^{3+}$ Ion and Its Spontaneous Hydration. Although treatment of *cis*-$[Co(en)_2(NH_2CH_2CN)Br]^{2+}$ with Hg^{2+} (vide supra) or OH^- ions[15] does not provide a route to the aqua– or hydroxo–nitrile species, oxidation of the coordinated Br with HOCl at ~0 °C results in a rapid violet to red color change, and from this solution *cis*-$[Co(en)_2(NH_2CH_2CN)(OH_2)](NO_3)_2ClO_4{\cdot}H_2O$ was isolated. (See eq 3.) Only a trace amount of the chelated


$$\left[(en)_2Co\begin{smallmatrix}NH_2CH_2CN\\ Br\end{smallmatrix}\right]^{2+} + HOCl + H^+ \longrightarrow \left[(en)_2Co\begin{smallmatrix}NH_2CH_2CN\\ OH_2\end{smallmatrix}\right]^{3+} + ClBr \quad (3)$$

amide $[Co(en)_2(glyNH_2)]^{3+}$ was sometimes observed, and this probably resulted from subsequent hydration of the aqua–nitrile species (vide infra). Elemental analysis, visible (ϵ_{484}(max) 80, ϵ_{351}(max) 74, Figure 2) and infrared (2246 cm^{-1} (s)) spectra, and reduction with $NaBH_4$ followed by thin-layer chromatography served to characterize the complex and show the continued presence of the nitrile. Similar treatment of $(+)_{589}$-$[Co(en)_2(NH_2CH_2CN)Br]Br_2$ resulted in the isolation of optically pure $(+)_{589}$-$[Co(en)_2(NH_2CH_2CN)(OH_2)](NO_3)_2ClO_4$ ($[M]_{589}$ 168° M^{-1} cm^{-1}, $[M]_{436}$ −1300° M^{-1} cm^{-1}), Figure 3, and it is clear that the rotatory dispersion curve of this ion is substantially less intense than that for $(-)_{589}$-$[Co(en)_2(glyNH_2)]^{3+}$. Titration with buffer solutions using a stopped-flow mixing device and extrapolation of the spectrophotometric traces to zero time established the pK_a for the process


$$\left[(en)_2Co\begin{smallmatrix}NH_2CH_2CN\\ OH_2\end{smallmatrix}\right]^{3+} + H_2O \rightleftharpoons \left[(en)_2Co\begin{smallmatrix}NH_2CH_2CN\\ OH\end{smallmatrix}\right]^{2+} + H_3O^+ \quad (4)$$

as 5.60 ± 0.05 (25 °C, μ = 1.0 M ($NaClO_4$)). This value is similar to that given above for the aqua–propionitrile species.

In neutral or alkaline solutions the aqua–aminoacetonitrile complex forms the chelated amide ion $[Co(en)_2(glyNH_2)]^{3+}$. The visible spectrum of the final solution (ϵ_{489}(max) 104, ϵ_{343}(max) 123) at pH 5.75 (imidazole or acetate buffer, 1 M $NaClO_4$) was indistinguishable from that of authentic *cis*-$[Co(en)_2(glyNH_2)]^{3+}$, and similar treatment of $(+)_{589}$-$[Co(en)_2(NH_2CH_2CN)(OH_2)]^{3+}$ (pH 5.2) gave, following quenching to pH ~3, a rotatory dispersion curve essentially that ($[M]_{589}$ 1360° M^{-1} cm^{-1}, $[M]_{465}$ −4625° M^{-1} cm^{-1}) of $(+)_{589}$-$[Co(en)_2(glyNH_2)]^{3+}$. Also, $[Co(en)_2(glyNH_2)](NO_3)_2ClO_4$ was isolated and was shown to be identical with the compound obtained following the treatment of $[Co(en)_2(glyNH_2)Br]^{2+}$ with Hg^{2+}.[22] An experiment carried out in the absence of Hg^{2+} but in 0.1 M $HClO_4$ showed no reaction after 10 days. Thus the aqua–nitrile is quite stable in acidic solutions.

The rate of amide formation was followed spectrophotometrically over the pH range 5–7.54 and the data, Table IV, agree with the rate law $v = k_1[Co(en)_2(NH_2CH_2CN)(OH)]^{2+} = k_1K_a[Co]_T/(K_a + [H^+])$ with $k_1 = 1.15 \times 10^{-2}$ s^{-1} and pK_a = 5.60. Figure 5 shows that the limiting rate $k_{obsd} = k_1$ is approached at pH 7, and the calculated value of K_a (2.51 × 10^{-6} M) agrees with the measured acid dissociation constant for the coordinated H_2O. Values for k_1 were also measured at 37 and 50 °C, Table IV, and the linear Arrhenius plot gave E_a = 11.3 kcal mol^{-1}, giving $\Delta H^{\ddagger}$ = 10.7 kcal mol^{-1} and $\Delta S^{\ddagger}$ = −31 cal deg^{-1} mol^{-1} at 25 °C.

Table IV. Spectrophotometric Rate Data[a] for the Uncatalyzed Hydration of *cis*-$[Co(en)_2(NH_2CH_2CN)(OH_2)]^{3+}$ at 25 °C, μ = 1.0 M ($NaClO_4$)

pH[b]	10^3k_{obsd}, s^{-1}	10^3k_{calcd},[c] s^{-1}
5.01	2.22	2.35
5.2[f]	4	
5.32	4.00	3.99
5.62	6.02	5.88
6.07	8.48	8.59
6.32	9.90	9.66
6.67	10.9	10.6
7.06	11.7	11.1
7.49	11.3	11.3
7.54	10.9	11.4
6.88[d]	25.7	25.2
7.34[d]	24.5	25.2
6.58[e]	44.7	
6.96[e]	53.7	52.0
7.20[e]	50.5	52.0

[a] Data collected at 474–488 nm and [Co] = (1–5) × 10^{-3} M. [b] Using 0.2 M imidazole-$HClO_4$ buffers. [c] $k_{calcd} = k_1K_a/(K_a + [H^+])$ with $k_1 = 1.15 \times 10^{-2}$ s^{-1} and pK_a = 5.60. [d] At 37 °C. [e] At 50 °C. [f] Polarimetric data using $(+)_{589}$-$[Co(en)_2(NH_2CH_2CN)(OH_2)](NO_3)_2ClO_4$.

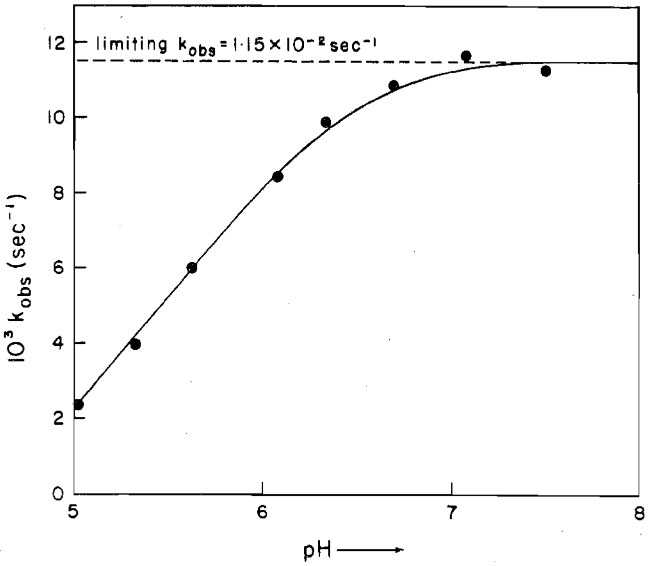


Figure 5. Plot of k_{obsd} vs. pH for the uncatalyzed cyclization of $[Co(en)_2(NH_2CH_2CN)(OH_2)](NO_3)_2ClO_4$; μ = 1.0 M ($NaClO_4$), 25 °C. The solid line represents k_{calcd} (see text).

Over the pH range 5–8.5 ion-exchange analysis of the reaction products (1 M $NaClO_4$, pH 8, borax buffer) showed that >95% of the product was $[Co(en)_2(glyNH_2)]^{3+}$ with <5% of a purple 2+ ion (2+ at pH 8, 3+ at pH 3) appearing at the higher pHs. An experiment in 0.1 M NaOH, however, yielded only the purple 2+ product (ϵ_{502}(max) ≃130, ϵ_{349}(max) ≃140, pH 8) and no chelated amide. This species, which was not investigated further, is probably the hydroxo–amidine complex $[Co(en)(N\text{-}(2\text{-aminoethyl})glycylamidine)(OH)]^{2+}$ formed by the OH^--catalyzed condensation between the nitrile and an amino group of an adjacent ethylenediamine residue. (See eq 5.) The spectral and chromatographic behaviors of this ion were similar to those obtained for one of the products formed in the base-catalyzed hydrolysis of $[Co(en)(amidine)Cl]^{2+}$.[25]

Since the intramolecular hydrolysis of coordinated amides and esters is catalyzed by phosphate anions,[2] the effect of phosphate in the nitrile hydration was looked at briefly. Data given in Table V show that 0.2 M phosphate buffer at pH 7.56 catalyzes the reaction of $[Co(en)_2(NH_2CH_2CN)(OH)]^{2+}$ about fivefold. Product analysis again indicated at least 95% of the product was the chelated amide. The observed rate law over the pH range 5.8–7.6 is approximately $v = (k_{hyd} +$

Table V. Spectrophotometric Rate Data[a] for the Phosphate-Catalyzed Hydration of *cis*-$[Co(en)_2(NH_2CH_2CN)(OH_2)]^{3+}$ at 25 °C, μ = 1.0 M ($NaClO_4$)

pH	10^3k_{obsd}, s^{-1}	$10^3(k_{obsd} - k_{hyd})$, s^{-1}	$10^2k_{HPO_4^{2-}}$,[b] s^{-1}	$[HPO_4^{2-}]$,[c] M	$k_{1(HPO_4^{2-})}$, $M^{-1}\ s^{-1}$
5.79	17.5	10.5	1.73	0.0352	0.49
6.77	42.4	31.5	3.36	0.134	0.25
7.22	60.0	48.5	4.97	0.170	0.29
7.56	76.5	65.0	6.57	0.185	0.35

[a] Data collected at 488 nm and [Co] = (1–5) × 10^{-3} M, with 0.2 M phosphate buffer. [b] Calculated using the expression rate = $(k_{hyd} + k_{HPO_4^{2-}})[CoOH] = (k_1 + k_{1(HPO_4^{2-})}[HPO_4^{2-}])K_a[Co]_T/(K_a + [H^+])$ with $k_1 = 1.15 \times 10^{-2}\ s^{-1}$ and $pK_a = 5.60$. [c] Calculated using $pK(H_3PO_4) = 1.68$, $pK(H_2PO_4^-) = 6.46$, and $pK(HPO_4^{2-}) = 11.1$.[45]

Table VI. Spectrophotometric Rate Data[a] for the Hg^{2+}-Catalyzed Intramolecular Nitrile Hydration of *cis*-$[Co(en)_2(NH_2CH_2CN)(OH_2)](NO_3)_2ClO_4$ at 25 °C, μ = 1.0 M ($NaClO_4$)[c]

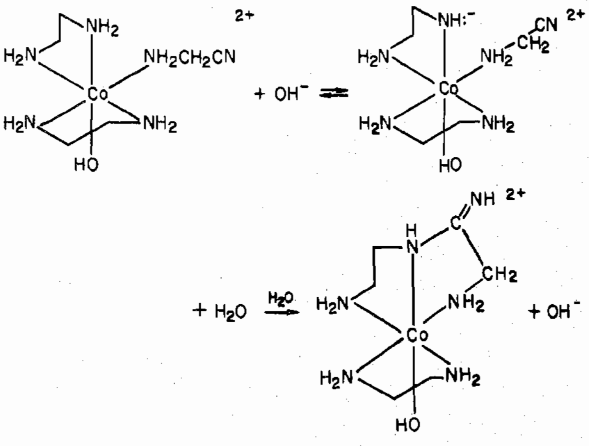
$[Hg^{2+}]$, M	$[H^+]$, M	10^2k_{obsd}, s^{-1}	$10^2k_{Hg^{2+}}$,[d] s^{-1}
0.10	0.10	44	44
0.05	0.10	23	46
0.04	0.10	18.8	47
0.02	0.10	9.70	48
0.01	0.10	4.94	49
0.01	0.10	4.6	46
0.01	0.10	4.8	48
0.01	0.055	9.3	51
0.01	0.01	41	41
0.005[b]	0.10	2.31	46
0.001[b]	0.10	0.42	42
0.0005[b]	0.10	0.180	36
0.0005[b]	0.10	0.194	39
0.5[c]	0.5	19.1	19.1
0.4[c]	0.5	10.0	12.5
0.2[c]	0.5	4.0	9.9
0.1[c]	0.5	1.92	9.6

[a] Followed at 470 and 345 nm; [Co] = (2.5–5.0) × 10^{-3} M. [b] [Co] = 1.0 × 10^{-3} M. [c] μ = 3.5 M ($NaClO_4$); $[H^+] = [HNO_3]$. [d] $k_{Hg^{2+}} = k_{obsd}[H^+]/[Hg^{2+}]$; see text.

Table VII. Spectrophotometric Rate Data[a] for Hg^{2+}-Catalyzed Intramolecular Nitrile Hydration of *cis*-$[Co(en)_2(NH_2CH_2CH_2CN)(OH_2)]^{3+}$ at 25 °C, μ = 1.0 M ($NaClO_4$)

$[Hg^{2+}]$, M	$[H^+]$, M	10^5k_{obsd}, s^{-1}	$10^5k_{Hg^{2+}}$,[b] s^{-1}
(a) Using Isolated *cis*-$[Co(en)_2(NH_2CH_2CH_2CN)(OH_2)](NO_3)_2(ClO_4)$			
0.2	0.05	24.3	6.1
0.2	0.08	16.5	6.6
0.2	0.10	12.0	6.0
0.1	0.05	13.1	6.5
0.1	0.05	13.7	6.8
0.05	0.05	6.6	6.6
0.1	0.10	6.62	6.6
0.05	0.10	3.18	6.4
0.025	0.10	1.50	6.0
(b) Following Rapid Br^- Removal from *cis*-$[Co(en)_2(NH_2CH_2CH_2CN)Br]Br_2$			
0.20	0.10	14.4	7.2
0.10	0.025	20.5	5.2
0.10	0.25	2.7	6.7
0.10	0.05	10.6	5.3
0.04	0.05	5.2	6.5

[a] Followed at 486, 490, or 350 nm; [Co] = (2–5) × 10^{-2} M. [b] $k_{Hg^{2+}} = k_{obsd}[H^+]/[Hg^{2+}]$; see text.



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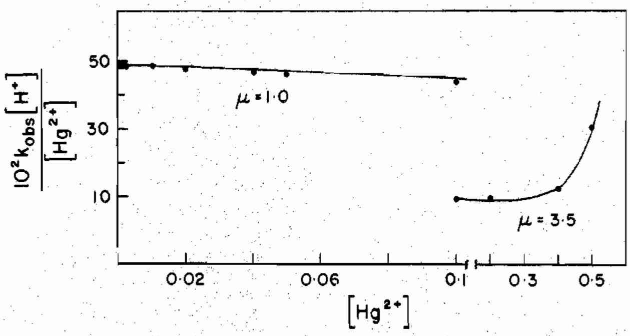


Figure 6. Plot of $k_{obsd}[H^+]/[Hg^{2+}]$ vs. $[Hg^{2+}]$ for the catalyzed cyclization of $[Co(en)_2(NH_2CH_2CN)(OH_2)](NO_3)_2ClO_4$; μ = 1.0 and 3.5 M ($NaClO_4$), 25 °C. The solid line gives k_{calcd} (see text).

$k_{HPO_4^{2-}}$)($[Co(en)_2(NH_2CH_2CN)(OH)]^{2+}$) = $(k_1 + k_{1(HPO_4^{2-})}[HPO_4^{2-}]K_a[Co]_T)/(K_a + [H^+])$. The calculated values of $k_{HPO_4^{2-}} = (k_{obsd} - k_{hyd})(1 + [H^+]/K_a)$, Table V, increase as the $[HPO_4^{2-}]$ is raised ($pK(H_2PO_4^-) = 6.46$) but $k_{HPO_4^{2-}}/[HPO_4^{2-}](k_{1(HPO_4^{2-})})$ is roughly constant. The variation probably reflects some uncertainty in the pK_a values under the conditions or possibly small contributions to the rate by other species ($H_2PO_4^-$, PO_4^{3-}).

Attempts to promote the similar formation of the six-membered β-alanine amide chelate using $[Co(en)_2(NH_2CH_2CH_2CN)(OH)]^{2+}$ were unsuccessful; no spectral change was observed over the pH range 6.6–7.6 in 832 h (0.2 M imidazole buffers), and no $[Co(en)_2(\beta\text{-alaNH}_2)]^{3+}$ was found by ion-exchange analysis. At 50 °C and pH 6.81 and 7.15, no 3+ product was observed after 8 h, and slow decomposition of the complex took place over 5 days at higher pH. In the presence of acetate buffers, some catalysis was suggested but this was not investigated further.

Hg^{2+}-Catalyzed Hydration in *cis*-$[Co(en)_2(NH_2CH_2CN)(OH)]^{2+}$ and *cis*-$[Co(en)_2(NH_2CH_2CH_2CN)(OH)]^{2+}$. Treatment of the isolated $[Co(en)_2(NH_2CH_2CN)(OH_2)](NO_3)_2ClO_4$ and $[Co(en)_2(NH_2CH_2CH_2CN)(OH_2)](NO_3)_2ClO_4$ complexes with Hg^{2+} in acidic solution results in the formation of the corresponding chelated amides $[Co(en)_2(glyNH_2)]^{3+}$ and $[Co(en)_2(\beta\text{-alaNH}_2)]^{3+}$, respectively. Spectral data and ion-exchange analysis show that both reactions are essentially quantitative (>95%) and no 2+ product is formed. Treatment of $(+)_{589}$-$[Co(en)_2(NH_2CH_2CN)$-

Table VIII. Spectrometric Rate Data[a] for the Ag^+-Catalyzed Intramolecular Nitrile Hydration of *cis*-$[Co(en)_2(NH_2CH_2CN)(OH_2)](NO_3)_2ClO_4$ at 25 °C, $\mu = 1.0$ M ($NaClO_4$)

$[Ag^+]$, M	$[H^+]$, M	10^3k_{obsd}, s^{-1}	10^3k_{calcd},[b] s^{-1}
0.9	0.10	41.5	4.61
0.85	0.10	38.3	4.51
0.7	0.10	29.1	4.15
0.6	0.10	23.0	3.83
0.4	0.10	12.6	3.15
0.3	0.10	8.43	2.81
0.2	0.10	4.62	2.31
0.15	0.10	2.93	1.95
0.10	0.10	1.68	1.68
0.10	0.01	15.8	1.58
0.10	0.005	30.5	1.53
0.05	0.10	0.615	1.23
0.05	0.01	5.97	1.19
0.05	0.005	11.9	1.19
0.01	0.10	0.0927	0.93
0.01	0.01	0.903	0.90
0.01	0.005	1.75	0.875

[a] At 488 and 345 nm; [Co] = (1.25–5) × 10^{-3} M. [b] $k_{calcd} = k_{obsd}[H^+]/[Ag^+]$.

$(OH_2)](NO_3)_2ClO_4$ ($[M]_{589} = 165°$ M^{-1} cm^{-1}) with 0.1 M Hg^{2+} in 0.05 M $HClO_4$ gives optically pure $(+)_{589}$-$[Co(en)_2(glyNH_2)]^{3+}$ ($[M]_{589} = 1660°$ M^{-1} cm^{-1}; $[M]_{465} = -5480°$ M^{-1} cm^{-1}), Figure 3.

The reaction of the aminoacetonitrile complex is rapid having $t_{1/2} \simeq 1.6$ s in 0.1 M Hg^{2+} (0.1 M $[H^+]$) while that for the aminopropionitrile complex is much slower, $t_{1/2} \simeq 3$ h under the same conditions. Rate data given in Tables VI and VII fit the rate law $k_{obsd} = k_{Hg^{2+}}[Hg^{2+}]/[H^+]$ with values of $k_{Hg^{2+}} = 0.48$ and 6.5×10^{-5} s^{-1} (25 °C, $\mu = 1.0$ M ($NaClO_4$)) for the two complexes. For $[Co(en)_2(NH_2CH_2CN)(OH_2)]^{3+}$ the rate is some 4 times slower at $\mu = 3.5$, and above 0.2 M Hg^{2+} $k_{Hg^{2+}}$ increases suggesting some contribution to the rate by a term more than first order in $[Hg^{2+}]$, Figure 6. For the aminopropionitrile complex similar rates were observed using the *cis*-$[Co(en)_2(NH_2CH_2CH_2CN)Br]^{2+}$ ion following the rapid removal of Br^-, Table VII.

To substantiate the intramolecular nature of the reaction, ^{18}O-enriched *cis*-$[Co(en)_2(NH_2CH_2CN)(^{18}OH_2)](NO_3)_2ClO_4$ ($\simeq$1.5 atom %) was treated with Hg^{2+} ion (0.02 M, 0.01 M H^+, 10 min) in isotopically normal water, and $[Co(en)_2(glyNH_2)](NO_3)_2ClO_4$ was recovered. Mass spectrometric analysis of the glycine amide moiety in this complex gave a [76]/[74] ratio for the amide peaks of about 2% indicating full retention of label during hydration.

Ag^+-Catalyzed Hydration in $[Co(en)_2(NH_2CH_2CN)(OH)]^{2+}$. As with the Hg^{2+}-catalyzed reaction, treatment of $[Co(en)_2(NH_2CH_2CN)(OH_2)](NO_3)_2ClO_4$ with $AgNO_3$ in acidic solution results in formation of the glycine amide species. Product analysis (ion exchange, visible spectra) showed that $[Co(en)_2(glyNH_2)]^{3+}$ is quantitatively formed; no $[Co(en)_2(NH_2CH_2CONH)]^{2+}$ was detected. The rate data given in Table VIII were obtained by repetitive scans from 600 to 300 nm and good isosbestic points occurred at 376, 404, and 536 nm (also observed in the Hg^{2+}-catalyzed reaction). At constant $[Ag^+]$ the data are inversely dependent on $[H^+]$, but in 0.1 M $HClO_4$ a complex Ag^+ dependence was observed with $k_{obsd}[H^+]/[Ag^+]$ increasing in a nonlinear fashion, Figure 7. The rate law over the $[Ag^+]$ range 0.01–0.9 M takes the form $k_{obsd} = (k_1'[Ag^+] + k_2'[Ag^+]^2)/[H^+](1 + K[Ag^+])$ with values of $k_1' = 0.8 \times 10^{-3}$ s^{-1}, $k_2' = 8 \times 10^{-3}$ M^{-1} s^{-1}, and $K = 1.3$ M^{-1} (25 °C, $\mu = 1.0$ M ($NaClO_4$)).

Zn^{2+}-, Cd^{2+}-, and Hg_2^{2+}-Catalyzed Hydration. One-tenth molar solutions of $Zn(NO_3)_2$ and $Cd(NO_3)_2$ also catalyzed hydration of *cis*-$[Co(en)_2(NH_2CH_2CN)(OH_2)]^{3+}$ (0.01 M $HClO_4$) although to a lesser extent than either Hg^{2+} or Ag^+. Reactions were first order in complex and the product spectra were identical with that of authentic $[Co(en)_2(glyNH_2)]^{3+}$ above 345 nm. Rate constants were 9.25×10^{-5} and 2.55×10^{-4} s^{-1} (25 °C, $\mu = 1.0$ M ($NaClO_4$)) for the Zn^{2+}- and Cd^{2+}-promoted reactions, respectively. For Hg_2^{2+} the data ($\mu = 3.5$ M), Table IX, show a constancy in $k_{obsd}[H^+]/[Hg_2^{2+}]$ from 0.05 to 0.25 M Hg_2^{2+} but increase at higher Hg_2^{2+} concentrations.

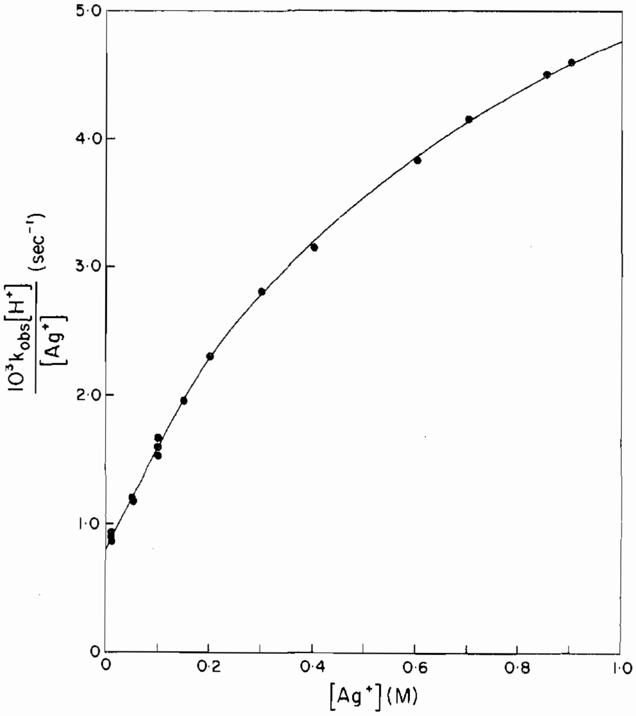


Figure 7. Plot of $k_{obsd}[H^+]/[Ag^+]$ vs. $[Ag^+]$ for the catalyzed cyclization of $[Co(en)_2(NH_2CH_2CN)(OH_2)](NO_3)_2ClO_4$; $\mu = 1.0$ M ($NaClO_4$), 25 °C. The solid line represents k_{calcd} (see text).

Table IX. Spectrophotometric Rate Data[a] for the Hg_2^{2+}-Catalyzed Intramolecular Nitrile Hydration of *cis*-$[Co(en)_2(NH_2CH_2CN)(OH_2)](NO_3)_2ClO_4$ at 25 °C, $\mu = 3.5$ M ($NaClO_4$)

$[Hg_2^{2+}]$, M	$10^2 \times k_{obsd}$, s^{-1}	$10^2 \times k_{calcd}$,[b] s^{-1}	$[Hg_2^{2+}]$, M	$10^2 \times k_{obsd}$, s^{-1}	$10^2 \times k_{calcd}$,[b] s^{-1}
0.5	10.08	10.1	0.20	1.98	4.95
0.4	5.5	6.87	0.10	0.97	4.85
0.25	2.48	4.95	0.05	0.50	5.00

[a] Followed at 485 nm; [Co] = 2.5 × 10^{-3} M; $[HNO_3]$ = 0.5 M. [b] $k_{calcd} = k_{obsd}[H^+]/[Hg_2^{2+}]$.

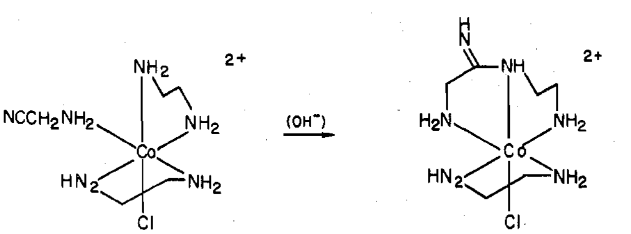
Hydration of Nitrile Complexes in Strong Acids. Dissolving *cis*-$[Co(en)_2(NH_2CH_2CN)Br]Br_2$ in concentrated HBr (9 M) at 25 °C slowly produced *cis*-$[Co(en)_2(glyNH_2)Br]^{2+}$. In 3 h >80% of the nitrile was converted to amide, as shown by ion-exchange analysis. Sampling after 5 min showed no hydration had occurred. In 2 M HBr at 25 °C little amide was produced in 6 days; in 2 M $HClO_4$ after 2 days there was no reaction.

The corresponding aminopropionitrile complex showed complete conversion to the *cis*-β-alanine amide complex after 2 days in 9 M HBr. If the reaction was stopped after ~18 h, about 50% of the nitrile was left unreacted.

Discussion

Synthesis and Configuration. The pentaamine complexes *cis*-$[Co(en)_2(NH_2(CH_2)_nCN)X]^{2+}$ (X = Cl, Br; n = 1, 2) were prepared by the method of Meisenheimer and Kiderlen[20] which routinely gives the cis isomer. The visible and ^{1}H NMR spectra agree with this assignment which was confirmed by the resolution of the aminoacetonitrile chloro and bromo ions into their catoptric forms using the (+)arsenyl tartrate anion.

The absolute configuration of $(+)_{589}$-$[Co(en)_2(NH_2CH_2CN)Cl]^{2+}$ is related to that of its base-catalyzed condensation product, Λ-$(+)_{589}$-[Co(en)(amidine)Cl]Cl_2. The absolute configuration of the latter complex is known from an x-ray study.[15,25] This reaction, which will be dealt with in detail in a subsequent paper,[25] does not involve the replacement or rearrangement of any of the coordinating atoms and is stereospecific for one of the amine centers.

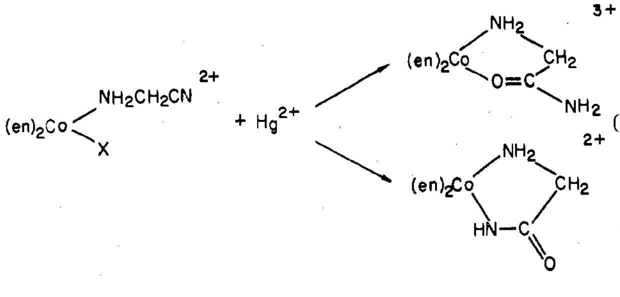


Λ-$(+)_{589}$ chloro nitrile ($[M]_{589} = 643° M^{-1} cm^{-1}$)

Λ-$(+)_{589}$ chloro amidine ($[M]_{589} = -2410° M^{-1} cm^{-1}$)

The absolute configurations of $(+)_{589}$-$[Co(en)_2(NH_2CH_2CN)Br]^{2+}$ and $(+)_{589}$-$[Co(en)_2(NH_2CH_2CH_2CN)X]^{2+}$ (X = Cl, Br) may be related by their rotatory dispersion curves, Figure 3, to that of Λ-$(+)_{589}$-$[Co(en)_2(NH_2CH_2CN)Cl]^{2+}$.[12] An independent assignment of configuration arises from a consideration of the products of the Hg^{2+}-catalyzed reactions of the $(+)_{589}$ chloro and bromo nitrile complexes. The rotatory dispersion curves of $(+)_{589}$-$[Co(en)_2(glyNH_2)]^{3+}$ and of $(+)_{589}$-$[Co(en)_2(\beta\text{-alaNH}_2)]^{3+}$ are similar and have the same overall form as those of Λ-$(+)_{589}$-$[Co(en)_2(sarO)]^{2+}$ (sarO = sarcosinate anion)[26] and Λ-$(+)_{589}$-$[Co(en)_2(l\text{-gluO})]^{2+}$ (*l*-gluO = *l*-glutamate anion).[27] The absolute configurations of the latter two complexes are known from x-ray investigations.[28,29] In amino acid complexes of this type, it appears that rotatory dispersion and circular dichroism curves are reliable guides to configurational relationships.

Hg^{2+}-Catalyzed Reactions. The two products formed in the reaction of Hg^{2+} with $[Co(en)_2(NH_2CH_2CN)X]^{2+}$ (X = Cl, Br) have been identified as the N–O and N–N chelated glycine amides (see eq 6). Hydrolysis of the nitrile does not precede removal of the halo group, and the two products are formed independently since they cannot be isomerized under the reaction conditions. Similar treatment of the propionitrile complex results in the initial formation of the aqua nitrile which subsequently undergoes Hg^{2+}-catalyzed hydrolysis to the β-alanine amide product (eq 7).



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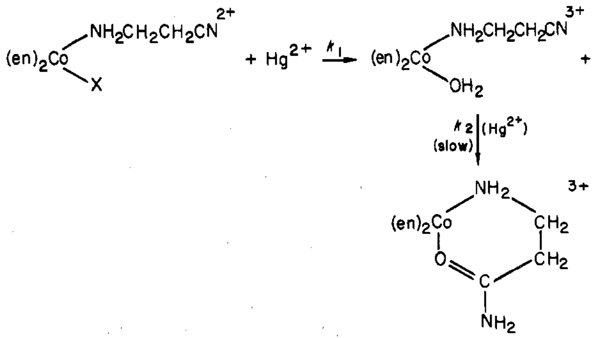

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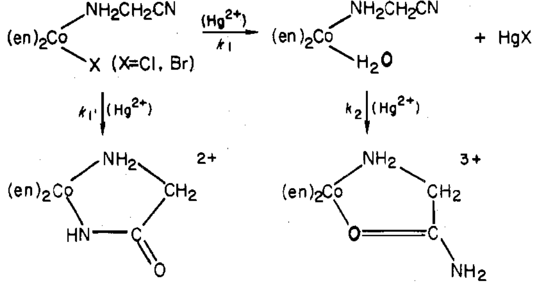
The similarity in the two reactants suggested that the aqua nitrile is probably formed as an intermediate in the aminoacetonitrile reaction with fast subsequent hydrolysis to the chelated glycine amide species. This was verified using the isolated aqua–aminoacetonitrile complex generated by the HOCl-induced oxidation of coordinated bromide.[30]

cis-$[Co(en)_2Br(NH_2CH_2CN)]^{2+}$ + HOCl + H^+

$\rightarrow$ *cis*-$[Co(en)_2(OH_2)(NH_2CH_2CN)]^{3+}$ + BrCl

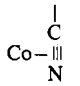
Hydrolysis in this species does not occur since it has been shown that the expected product, the aqua–glycinamide complex, does not subsequently form $[Co(en)_2(glyNH_2)]^{3+}$ but rather undergoes intramolecular hydrolysis to the $[Co(en)_2(glyO)]^{2+}$ ion.[2] Thus the aqua nitrile is required to undergo a concerted hydrolysis–chelation process, and the intramolecular involvement of the coordinated water has been demonstrated using ^{18}O-enriched *cis*-$[Co(en)_2(NH_2CH_2CN)(OH_2)](NO_3)_2ClO_4$. Also, since the N–N bound glycine imide species is not produced from the aqua nitrile and the chloro– and bromo–aminoacetonitrile complexes give significantly different amounts of it, reaction 6 may be rewritten as



(8)

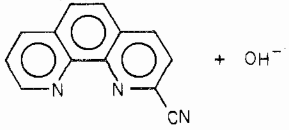
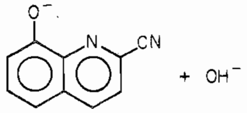
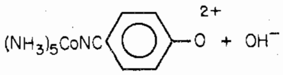
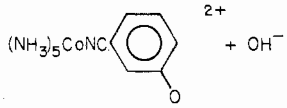
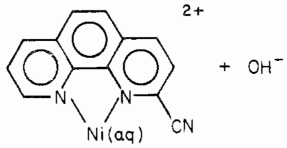
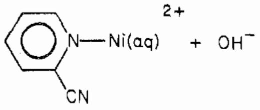
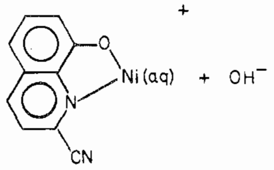
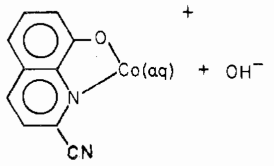
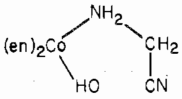
The mechanistic aspects of these separate processes will now be considered in detail.

(a) Removal of Halide. The first-order dependence on Hg^{2+} for the bromo–aminoacetonitrile complex indicates that the ion pair $[Co(en)_2(NH_2CH_2CN)Br]^{2+}$, Hg^{2+} is not important at $[Hg^{2+}] = 0.5$ M ($K_{IP} < 1$). This is in agreement with other studies on 2+ cationic complexes although saturation kinetics have been approached for the lower charged *cis*-$[Co(en)_2Cl_2]^+$ and α-$[Co(eee)Cl_2]^+$ species.[31] Since the amide:imide product ratio is independent of $[Hg^{2+}]$, both processes are Hg^{2+} catalyzed. However, since the amount of imide produced is dependent on the leaving group (Br > Cl), this part of the reaction at least does not involve a common intermediate. Good evidence exists for a common intermediate in the Hg^{2+}- and NO^+-induced aquations of the similar amine complexes *cis*-$[Co(en)_2(NH_3)X]^{2+}$ (X = Cl, Br, N_3)[32] and for more diverse leaving groups in the $(NH_3)_5CoX^{2+}$ species (Cl, Br, I[33] with Hg^{2+}; N_3,[33,34] NCO,[35] $OCONH_2$[36] with NO^+; and N_3[37] with e_{aq}^-), and it is proposed that the bulk of the present reaction incorporates a similar five-coordinate intermediate. For the imide product it is possible that the alternative "side-on" binding of Hg^{2+} to the nitrile leads to the synergistic entry of nitrile as HgX^+ leaves. The resultant



species would hydrate rapidly and it could also dissociate to the five-coordinate intermediate. (See Scheme I.) The

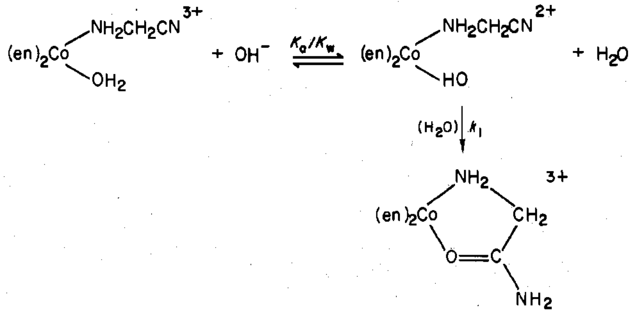
Table X. Comparisons of Rates and Activation Parameters for Uncatalyzed and Metal-Promoted Nitrile Hydration

Reaction	k(25 °C), $M^{-1}\ s^{-1}$ or s^{-1}	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, cal $deg^{-1}\ mol^{-1}$	Ref
$CH_3CN + OH^-$	1.6×10^{-6}			12
$CH_3CH_2CN + OH^-$	4×10^{-6}	19.7	−18	39
$C_6H_5CN + OH^-$	8.2×10^{-6}	19.9	−15	40,[a] 10
p-$ClC_6H_4CN + OH^-$	7.2×10^{-6}	17.4	−19	40,[a] 10
	2.6×10^{-3}	15.7	−20	7
	1.1×10^{-3}	13.4	−27	38
$(NH_3)_5CoNCCH_3{}^{3+} + OH^-$	3.4			12
$(NH_3)_5CoNCC_6H_5 + OH^-$	18.8	16.5	+3	10
	0.2	16.3	−7(±4)	10
	3.6	15.1	−6(±4)	10
	2.4×10^{4}	15.1	+14	7
	6.3×10^{7}	13.7	+23	41
	1.6×10^{2}	14.2	−1	38
	50	14.3	−3	38
	1.15×10^{-2}	10.7	−31	This work

[a] Recalculated by Pinnell, Wright, and Jordan.[10]

significantly slower rate for the reaction ($k_{Hg} = 0.12\ M^{-1}\ s^{-1}$) compared with other bromo amines (Table II, $k_{Hg} = 2.4$–$7.9\ M^{-1}\ s^{-1}$) can be accommodated by an intermediate complex of the type $[Co(en)_2(NH_2CH_2CNHg)X]^{4+}$ containing nitrile-bound Hg^{2+}; the less electrophilic $-CNHg^{2+}$ moiety would provide for the slower displacement of X and possibly for the direct entry of N-bound nitrile via initial coordination to the carbon atom of the nitrile.

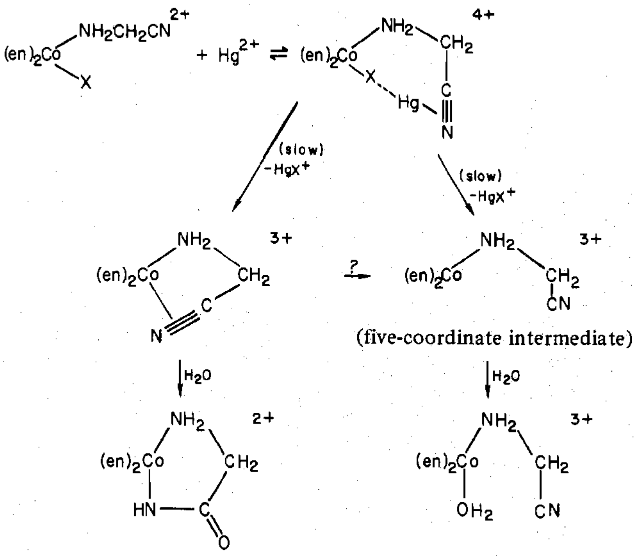
(b) Spontaneous Hydrolysis of the Cis Aquo–Nitrile Complexes. The cis aquo–aminoacetonitrile complex undergoes base-catalyzed hydrolysis to the chelated glycine amide species, and the rate law $k_{obsd} = k_1K_a/(K_a + [H^+])$ supports the attack of coordinated hydroxide as the rate-determining step. Although the direct incorporation of the bound hydroxo group has not been directly demonstrated by ^{18}O-tracer studies, the rapidity of the reaction and its similarity to the Hg^{2+}-catalyzed process in which the direct involvement of the coordinated hydroxo group has been demonstrated strongly imply a direct intramolecular process. The limiting rate k_1 ($1.15 \times 10^{-2}\ s^{-1}$) occurs at pH >7. The thermodynamic parameters are compared with those for some related bimolecular reactions in Table X and two comments seem appropriate. First, direct coordination of the nitrile to the metal center (Co(III) complexes) results in a decrease in $\Delta H^{\ddagger}$ (by ~3 kcal mol^{-1}) and an increase in $\Delta S^{\ddagger}$ (15–20 eu) both factors contributing to a rate acceleration of ~10^6; for the Co(II)[38] and Ni(II)[7,38] complexes of 2-cyanophenanthroline



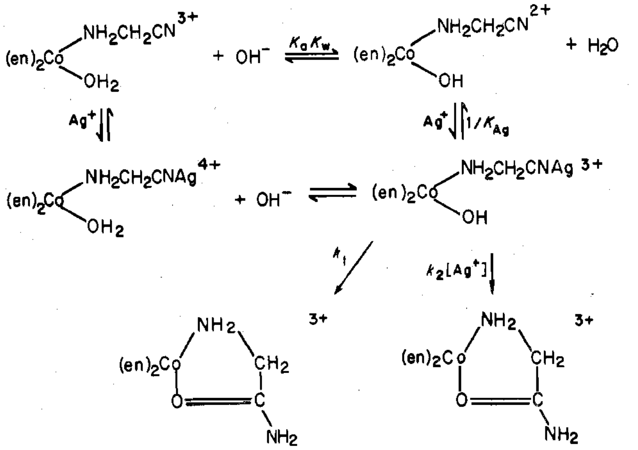
and 2-cyano-8-hydroxyquinoline the rate acceleration of 10^5–10^7 results entirely from an increase in $\Delta S^\ddagger$ (25–34 eu). This large entropic change probably results from charge neutralization in the addition complex and the resultant desolvation of the OH^- ion. In the intramolecular process, however, charge neutralization and desolvation of OH^- are apparent in the reactant complex $[Co(en)_2(NH_2CH_2CN)(OH)]^{2+}$, and consequently $\Delta S^\ddagger$ is again large and negative. The rate acceleration now resides entirely in the 9 kcal mol^{-1} decrease in $\Delta H^\ddagger$ (10^6 in rate). This 13-eu decrease in $\Delta S^\ddagger$ for the intramolecular process is also found in the hydrolysis of propionic anhydride by coordinated hydroxide in $(NH_3)_5CoOH^{2+}$.[46] This agreement suggests that desolvation of hydroxide resulting in entropic rate retardations of 10^2–10^3 may well be a common property of coordinated hydroxide in both bimolecular and intramolecular hydrolysis (or hydration) processes.

(c) Metal Ion Catalyzed Hydration of the Aquo–Nitrile Complexes. The Ag^+-catalyzed reaction clearly involves a strong dependence on a term in $[Ag^+]^2$ and this may be accommodated by the mechanism shown in Scheme II. The derived rate law takes the form $k_{calcd} = K_aK_{Ag}[Ag^+](k_1 + k_2[Ag^+])/[H^+](1 + K_{Ag}[Ag^+])$ and this agrees with the observed rate law with $k_1' = k_1K_aK_{Ag}$ and $k_2' = k_2K_aK_{Ag}$. A general least-squares fit of the data[42] using the measured value of K_a (2.5×10^{-6} M) gives $K_{Ag} = 1.26$ M^{-1}, $k_1 = 2.56 \times 10^2$ s^{-1}, and $k_2 = 3.16 \times 10^3$ M^{-1} s^{-1}. The least-squares fit is depicted by the solid line in Figure 7. The value of K_{Ag} compares favorably with a value of 5.6 M^{-1} for the association of Ag^+ with acetonitrile in water;[43] it is apparent that at low $[Ag^+]$ a strong dependence on $[Ag^+]^2$ occurs with the k_1 path contributing only about 30% at $[Ag^+] = 0.25$ M. At the highest silver concentration (0.9 M) when association with the first Ag^+ ion becomes almost saturated ($K_{Ag}[Ag^+] > 1$), the observed rate reverts to a first order in Ag^+ dependence.

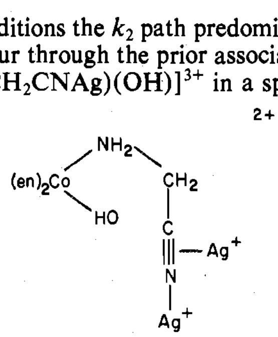
Scheme I



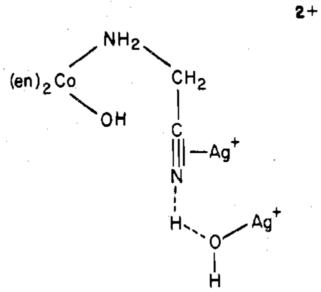
Scheme II



Under these conditions the k_2 path predominates. This latter process may occur through the prior association of Ag^+ with $[Co(en)_2(NH_2CH_2CNAg)(OH)]^{3+}$ in a species such as



or it may involve a transition state in which the second Ag^+ acts as a general acid in aiding protonation of the nitrile



Whatever the precise mechanism, two Ag^+ ions are jointly involved in activation of the nitrile toward intramolecular attack by the coordinated hydroxo group.

A similar process is likely for the Hg^{2+}-promoted intramolecular reaction, but the data require catalysis by a second Hg^{2+} ion to be unimportant below 0.4 M. (See Scheme III.) This is perhaps reasonable in view of the higher overall charge on both $[Co(en)_2(NH_2CH_2CNHg)(OH)]^{4+}$ and Hg^{2+}. Provided $K_{Hg}[Hg^{2+}] < 1$, the derived rate expression takes the form $k_{calcd} = K_aK_{Hg}[Hg^{2+}](k_1 + k_2[Hg^{2+}])/[H^+]$ which agrees with the observed rate law with $k_{Hg^{2+}} = k_1K_aK_{Hg} = 0.48$ s^{-1} for the aminoacetonitrile complex and 6.5×10^{-5} s^{-1} for the aminopropionitrile complex. Since saturation kinetics were not observed, it is not possible to derive the unimolecular rate for hydration in $[Co(en)_2(NH_2CH_2CNHg)(OH)]^{4+}$. However, assuming $K_{Hg} = 0.1$ M^{-1}, $k_1 = 5 \times 10^5$ s^{-1} for formation of the five-membered chelate and 60 s^{-1} for the six-membered β-alanine amide complex. Stability constants for the binding of Hg^{2+} to nitriles have not been reported, but free energies of transfer of Zn^{2+}, Cd^{2+}, and Ag^+ from water to acetonitrile[44] suggest that the binding of Hg^{2+} to nitriles will be somewhat smaller than that found for Ag^+.[43]

Although the Hg_2^{2+}-, Zn^{2+}-, and Cd^{2+}-catalyzed reactions have not been investigated in detail, estimates of their relative efficiencies are possible and are given in Table XI. In obtaining these data it is assumed that the hydroxo complex is

Scheme III

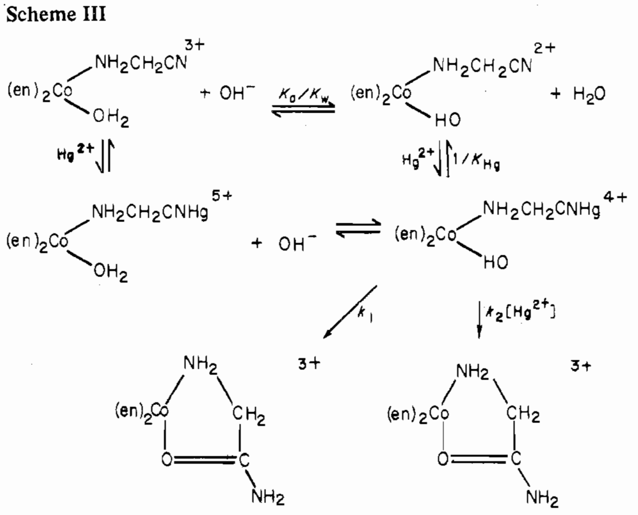
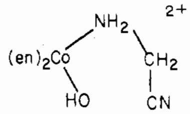
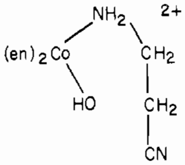
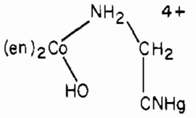
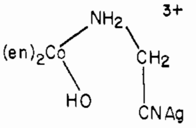
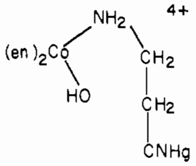


Table XI. Comparisons of Catalysis by Metal Ions in the Hydration of $[Co(en)_2(NH_2CH_2CN)(OH)]^{2+}$

Metal ion	$k_{obsd}[H^+]/[M^{2+}]$, s^{-1}	Rel rate	Metal ion	$k_{obsd}[H^+]/[M^{2+}]$, s^{-1}	Rel rate
None	3×10^{-8} [a]	1	Hg^{2+}	48×10^{-2}	1.6×10^7
Zn^{2+}	9×10^{-6}	3×10^2	Hg_2^{2+}	25×10^{-2} [b]	10^7
Cd^{2+}	2.5×10^{-5}	10^3	Ag^+	8×10^{-4}	3×10^4

[a] k_{obsd} calculated at $[H^+] = 1.0$ M. [b] Calculated assuming a 5× rate increase from $\mu = 3.5$ to $\mu = 1.0$ M.

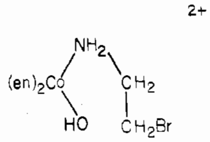
Table XII. Rate Comparisons for the Formation of Five- and Six-Membered Chelated Amides

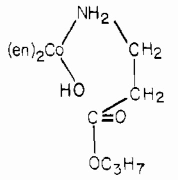
Compd	k(25 °C), s^{-1}	Rel rate (pH 7)
	1.15×10^{-2}	1
	$<10^{-7}$	$<10^{-5}$
	5×10^5 [a]	5×10^7
	60	6×10^3
	~60[a]	6×10^3

[a] Calculated assuming $K_{Hg^{2+}} = 0.1$ (see text).

the reactive species in each case and that a first-order dependence on $[M^{2+}]$ occurs for Zn^{2+} and Cd^{2+}. It is apparent that Zn^{2+} and Cd^{2+} are less effective than Hg^{2+}, Hg_2^{2+}, or Ag^+. Although association constants for these metals with nitriles have not been reported, it is likely that the slower overall reactions result from smaller $K_{M^{2+}}$ values rather than from a marked reduction in k_1.

Finally, it is of interest to compare the relative efficiencies for cyclization to give the five- and six-membered chelates. Such comparisons are given in Table XII. The large rate difference found in the absence of any additional activation (>10^5) is maintained, or moderated only slightly, by the presence of Hg^{2+} (~10^4) and it is interesting that Hg^{2+} catalyzes this process much more than Ag^+ (~10^4) or the other metals. Thus the combination of the intramolecular process and Hg^{2+} activation results in an acceleration in hydration of the uncoordinated nitrile at pH 7 of about 10^{18} (Tables X and XII). Similar comparisons are not yet available for cyclizations in the related esters or amides although it is of interest that the first-order rate for hydration of the acetonitrile complex is not much faster than the rate for lysis of Br^- in the corresponding ion and that the lack of hydration of the propionitrile complex may be compared with a rate of attack of coordinated hydroxide in excess of 0.1 s^{-1} in the corresponding ester[19] However, further studies are needed before such differences can be adequately rationalized.





Acknowledgment. We thank Dr. J. MacLeod of this school for running the mass spectrograms and Mr. M. Wein for carrying out numerous check experiments long after the major portions of this work had been completed.

Registry No. *trans*-$[Co(en)_2Br_2]Br$, 15005-14-8; *cis*-$[Co(en)_2Br(NH_2CH_2CN)]Br_2$, 62301-95-5; *cis*-$[Co(en)_2Br(NH_2CH_2CN)](ClO_4)_2$, 62301-94-4; $(-)_{589}$-$[Co(en)_2(NH_2CH_2CN)Br]Br_2$, 62357-26-0; $(+)_{589}$-$[Co(en)_2(NH_2CH_2CN)Br]Br_2$, 62357-27-1; *trans*-$[Co(en)_2Cl_2]Cl$, 14040-33-6; *cis*-$[Co(en)_2Cl(NH_2CH_2CN)]Cl_2$, 27592-47-8; $(+)_{589}$-$[Co(en)_2(NH_2CH_2CN)Cl](As_2C_8O_{12}H_4)$, 62357-25-9; $(+)_{589}$-$[Co(en)_2(NH_2CH_2CN)Cl]Br_2$, 62357-23-7; $(-)_{589}$-$[Co(en)_2(NH_2CH_2CN)Cl]Br_2$, 62357-22-6; *cis*-$[Co(en)_2Br(NH_2CH_2CH_2CN)]Br_2$, 62301-93-3; *cis*-$[Co(en)_2(OH_2)(NH_2CH_2CN)](NO_3)_2(ClO_4)$, 62357-21-5; *cis*-$[Co(en)_2(OH_2)(NH_2CH_2CH_2CN)](NO_3)_2(ClO_4)$, 40215-52-9; *cis*-$[Co(en)_2Br(\beta\text{-alaNH}_2)]Br_2$, 62301-92-2; $[Co(en)_2(\beta\text{-alaNH}_2)](ClO_4)_3$, 62319-90-8; *cis*-$[Co(en)_2(^{18}OH_2)(NH_2CH_2CN)](NO_3)_2(ClO_4)$, 62301-91-1; $[Co(en)_2(glyNH_2)](NO_3)_2(ClO_4)$, 62319-87-3; $[Co(en)_2(NH_2CH_2CONH)](NO_3)_2$, 62319-88-4; *cis*-$[Co(en)_2(NH_2CH_2CN)Br]^{2+}$, 39210-04-3; *cis*-$[Co(en)_2(NH_2CH_2CN)Cl]^{2+}$, 46240-53-3; *cis*-$[Co(en)_2(NH_2CH_2CH_2ON)Br]^{2+}$, 39210-05-4; Hg^{2+}, 14302-87-5; *cis*-$[Co(en)_2(NH_2CH_2CN)(OH_2)]^{3+}$, 62357-20-4; $(+)_{589}$-$[Co(en)_2(NH_2CH_2CN)(OH_2)]^{3+}$, 62301-88-6; $(+)_{589}$-$[Co(en)_2(NH_2CH_2CN)(OH_2)](NO_3)_2ClO_4$, 62301-89-7; HPO_4^{2-}, 29505-79-1; Cd^{2+}, 22537-48-0; Hg_2^{2+}, 12596-26-8; Zn^{2+}, 23713-49-7; Ag^+, 14701-21-4; *cis*-$[Co(en)_2(NH_2CH_2CH_2CN)(OH_2)]^{3+}$, 46361-78-8; $(+)_{589}$-$[Co(en)_2(glyNH_2)]^{3+}$, 62357-85-1; *cis*-$[Co(en)_2Br(NH_3)](ClO_4)_2$, 62301-87-5; *cis*-$[Co(en)_2Br(NH_2CH_3)](ClO_4)_2$, 62301-86-4; *cis*-$[Co(en)_2Br(NH_2CH_2CO_2CH_3)](ClO_4)_2$, 23242-57-1; *cis*-$[Co(en)_2Br(NH_2CH_2CO_2C_2H_5)](ClO_4)_2$, 49567-52-4; *cis*-$[Co(en)_2Br(NH_2CH_2CH_2CO_2C_3H_7)](ClO_4)_2$, 62301-85-3; *cis*-$[Co(en)_2Br(NH_2CH_2CH_2CO_2H)](ClO_4)_2$, 62301-83-1; *cis*$[Co(en)_2Br(NH_2CH_2CO_2C_3H_7)](ClO_4)_2$, 62301-81-9; $[Co(en)_2(NH_2CH_2C(OH)(NH))](ClO_4)_3$, 62319-86-2; $[Co(en)_2(NH_2CH_2CONH)](ClO_4)_2$, 62319-85-1.

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Reactions of μ-Diphenylethyne-hexacarbonyldicobalt with Bis(diphenylphosphino)methane and Bis(diphenylarsino)methane. Crystal Structures of (tolan)(dpm)Co$_2$(CO)$_4$ and (tolan)(dam)$_2$Co$_2$(CO)$_2$·C$_2$H$_4$Cl$_2$

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The bidentate ligands bis(diphenylphosphino)methane (dpm) and bis(diphenylarsino)methane (dam) displace two or four carbonyl groups from μ-tolan-hexacarbonyldicobalt, (tolan)(CO)$_6$Co$_2$ (tolan = diphenylethyne). Single-crystal x-ray diffraction studies have yielded the molecular geometries of μ-bis(diphenylphosphino)methane-μ-tolan-tetracarbonyldicobalt and di-μ-bis(diphenylarsino)methane-μ-tolan-dicarbonyldicobalt. The crystal data for the phosphino complex (tolan)(dpm)Co$_2$(CO)$_4$ are as follows: space group $P2_1/n$ (C_{2h}^5; No. 14, nonstandard setting) with $a = 19.97$ (2) Å, $b = 20.41$ (2) Å, $c = 15.45$ (2) Å, $\beta = 97.57$ (7)°, $V = 3742$ Å^3, $Z = 4$. A unique quadrant of 3144 diffraction intensities with $I > 3\sigma(I)$ and $2\theta < 40°$ (Mo Kα radiation), collected on a Picker FACS-1 diffractometer, was used to solve and refine the structure by conventional Patterson, Fourier, and full-matrix least-squares techniques. Phenyl groups were constrained as idealized rigid groups with isotropic thermal parameters; remaining atoms were refined anisotropically to final discrepancy indices $R_F = 0.088$ and $R_{wF} = 0.102$. The bidentate phosphine ligand bridges between the cobalt atoms. The cobalt–cobalt bond length is 2.459 (2) Å and the cobalt–phosphorus bond lengths are 2.210 (3) and 2.215 (3) Å, while those from cobalt to "acetylene" carbon atoms are 1.97 (1), 1.95 (1), 1.94 (1), and 1.92 (1) Å. The carbon–carbon distance is 1.33 (1) Å. The arsino complex (tolan)(dam)$_2$Co$_2$(CO)$_2$ was crystallized as the dichloroethane monosolvate: space group $P\bar{1}$ (C_i^1, No. 2) with $a = 14.207$ (4) Å, $b = 17.321$ (5) Å, $c = 13.736$ (4) Å, $\alpha = 73.63$ (2)°, $\beta = 112.44$ (2)°, $\gamma = 99.78$ (2)°, $V = 2990$ Å^3, $Z = 2$. Structure solution and refinement employed 4158 intensities measured in a unique hemisphere on the diffractometer ($I > 3\sigma(I)$ and $2\theta < 40°$ using Mo Kα radiation). Refinement with rigid rings was terminated with $R_F = 0.086$ and $R_{wF} = 0.075$. The arsine ligands both bridge between the cobalt atoms which are 2.518 (4) Å apart. Cobalt–arsenic bond lengths are 2.326 (4), 2.330 (4), 2.332 (4), and 2.348 (3) Å. The cobalt to "acetylene" carbon distances are 1.97 (1), 1.98 (1), 1.95 (1), and 1.95 (1) Å while the carbon–carbon distance is 1.37 (3) Å.

Introduction

The replacement of up to two carbonyl groups on alkynehexacarbonyldicobalt is facile with a large range of ligands.[1] To progress beyond two, monodentate ligands must have good π-acceptor properties. Thus trialkyl or triaryl phosphites[2] or trifluorophosphine[3] replaces a maximum of four carbonyl groups. The preparation of complexes in which two carbonyl groups have been replaced by a bridging ligand has been