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Reactivity of Coordinated Nitriles

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Abstract: The base hydrolysis of coordinated acrylonitrile in $[(NH_3)_5CoN{\equiv}CCH{=}CH_2]^{3+}$ to the acrylamide complex in carbonate buffers obeys the rate law $k_{obsd} = k_{OH}[OH^-] + k_c[CO_3^{2-}]$ ($k_{OH} = 35\ M^{-1}\ s^{-1}$; $k_c = 1\ M^{-1}\ s^{-1}$; 25 °C, $\mu = 1.0$), and ^{18}O tracer studies indicate the mechanism of hydrolsis by carbonate ion to involve direct nucleophilic attack at the nitrile group by CO_3^{2-} with subsequent elimination of CO_2. Coordination of malononitrile, cyanoacetic acid, and ethyl cyanoacetate to the $(NH_3)_5Co^{III}$ moiety leads to greatly increased acidity of the methylene protons (pK_a of $[(NH_3)_5CoN{\equiv}CCH_2C{\equiv}N]^{3+}$ is 5.7 ± 0.1 ($\mu = 1.0$, 25 °C) compared with 11.3 for uncoordinated malononitrile). In basic aqueous solutions, these complexes equilibrate rapidly between the original complexes and the complexes containing the deprotonated activated methylene group. The protonated complexes then hydrolyze to the coordinated amides with both hydroxide ion and water acting as nucleophiles while the coordinated carbanions undergo an intramolecular electron transfer of a single electron to yield Co(II) and the ligand radical. The C-deprotonated complexes also function as nucleophiles for appropriate substrates (such as methyl iodide, methyl pyruvate, or bromine) to form the corresponding substituted species. In nonaqueous media, generation of the ligand radical initiates polymerizations of monomers methacrylate, styrene, acrylonitrile, and methacrylonitrile by a radical (rather than an ionic) mechanism.

Increased reactivity of coordinated nitriles has been observed on a number of occasions.[1-7] Marked acceleration in the rates of hydrolysis to the amide by OH^- compared with the uncoordinated species has been recorded both for inter- and intramolecular hydrolysis processes. The acceleratory effect for coordinated acetonitrile was also accompanied by an enhancement in the rate of proton exchange for the methyl group: in fact, the latter process was slightly faster than OH^- attack at the nitrile carbon.[6] This property is in accord with some earlier observations on the treatment of $[(NH_3)_5Co(NCCH_2CN)]^{3+}$ with base.[8] A solution of this latter ion in water gave an intense red color when OH^- was added. The color faded gradually to give a yellow solution similar in appearance to the original solution, although the visible spectra were not identical. The initial observation was attributed to deprotonation of the acidic methylene group, but the second reaction was not investigated further.[8] If the interpretation of the initial reaction is correct, the acidity of coordinated malononitrile is considerably greater than that of the uncoordinated species, and this paper reports on the hydrolysis and reactivity of such nitrile complexes. Studies on several related nitriles have also been made.

Experimental Section

Electronic spectra and molar absorptivities ϵ ($M^{-1}\ cm^{-1}$) were recorded by using a Cary 118C spectrophotometer, ^1H NMR spectra by using either a Varian HA-100 or a JEOL MH-100 spectrometer, and IR spectra by using a Perkin-Elmer PE 225 spectrometer with KBr disks (ca. 5 mg of complex/200 mg of KBr).

Synthesis and Reagents. Cyanoacetic acid (Unilab), ethyl cyanoacetate (Fluka, puriss), trimethyl phosphate (Pflaum), nitrosyl tetrafluoroborate (Ozark-Mahoning), and acrylonitrile (Aldrich) were used without further purification. Malononitrile (Pfaltz and Bauer) was freshly distilled before use (76–77 °C, (1 mmHg)). $[Co(NH_3)_5N_3]Cl_2$ was converted to the tetrafluoroborate salt by using $AgOOCCH_3/NaBF_4$, and $[Co(NH_3)_5(OP(OCH_3)_3)](BF_4)_3$ was isolated in an analogous way to that of $[Co(NH_3)_5(OP(OC_2H_5)_3](ClO_4)_3$[8] by using the corresponding BF_4^- salts. Nitrosyl triflate was prepared by passing N_2O_3 gas (from $H_2SO_4/NaNO_2$) into purified CF_3SO_3H until crystallization was complete.

$[Co(NH_3)_5(N{\equiv}C\text{-}CH_2C{\equiv}N)](ClO_4)_3$. $[Co(NH_3)_5(OP(OCH_3)_3)](BF_4)_3$ (4.0 g) was dissolved in freshly distilled malononitrile (50 mL) and concentrated H_2SO_4 (0.5 mL) added. The mixture was maintained at ca. 50 °C until it turned yellow (ca. 3 h). Ethanol (50 mL) and ether (300 mL) were added, the solution was filtered and the product was washed with ethanol and acetone and air dried. The resultant complex (3.0 g, 80%) was purified by dissolution in 0.1 M HBr (50 mL) and adding excess LiBr (ca. 5 g) to remove any amide complex. The solution was cooled quickly and filtered, and excess solid $NaClO_4$ was added to the filtrate whereupon $[Co(NH_3)_5(N{\equiv}CCH_2C{\equiv}N)](ClO_4)_3$ crystallized out. This material was further recrystallized by precipitation using $NaClO_4$ from a 0.1 M $HClO_4$ solution and was collected as indicated above. Yield: 1.9 g, 51%.

A solution in 0.01 M $HClO_4$, measured rapidly after dissolution, gave two maxima in the visible spectrum ($\epsilon_{474} = 72$, $\epsilon_{341} = 82$). The infrared spectrum showed two absorptions at 2263 and 2330 cm^{-1}, attributed to the $-C{\equiv}N$ stretching modes of the terminal and bound $-CN$ groups, respectively. Anal. Calcd for $[Co(NH_3)_5NCCH_2CN](ClO_4)_3$: Co, 11.6; C, 7.09; H, 3.37;, N, 19.3. Found: Co, 11.7; C, 7.3; H, 3.6; N, 19.4.

$[Co(NH_3)_5(N{\equiv}CCH_2CO_2C_2H_5)](ClO_4)_3$. $[Co(NH_3)_5N_3](BF_4)_2$ (2.0 g), ethyl cyanoacetate (30 mL), and trimethyl phosphate (10 mL, to affect dissolution) were stirred, and excess $NOBF_4$ was added slowly. The mixture was stirred for a further 2 h, and the complex (as the BF_4^- salt) was precipitated by using ether. The product was recrystallized twice by precipitation using $NaClO_4$ from solutions in slightly acidified water. It was washed with ethanol and ether and air-dried. Yield: 0.8 g, 26%.

The visible spectrum (0.01 M $HClO_4$) showed two maxima ($\epsilon_{465} = 64$, $\epsilon_{295} = 89$), and the infrared spectrum (KBr disk) indicated $\nu_{CN} = 2325$ cm^{-1}. Anal. Calcd for $[Co(NH_3)_5(NCCH_2CO_2C_2H_5)](ClO_4)_3$: Co, 10.6; C, 10.8; H, 3.99; N, 15.1. Found: Co, 10.8; C, 10.7; H, 4.1; N, 15.1.

A much higher yield was obtained by adding NOO_3SCF_3 (8 g) to a vigorously stirred solution of $[(NH_3)_5CoN_3](CF_3SO_3)_2$ (15 g) in acetone (20 mL) and $NCCH_2COOC_2H_5$ (100 mL). Only a little complex remained undissolved in this solvent mixture. The solution rapidly turned yellow-brown as N_2 and N_2O evolution occurred, and after 15 min a copious yellow precipitate had appeared. The mixture was cooled at 0 °C for 30 min and then mixed with ether (100 mL) and the product collected. The triflate salt was recrystallized from CH_3OH by addition of ether to give fine needles (17 g).

$[Co(NH_3)_5(N{\equiv}CC(CH_3)_2CO_2C_2H_5)](NO_3)_3$. $[Co(NH_3)_5(NCCH_2CO_2C_2H_5)](ClO_4)_3$ (0.36 g) was dissolved in dry Me_2SO (10 mL), and MeI (ca. 1 mL) was added, followed immediately by imidazole (0.10 g). The mixture was shaken, stoppered, and left to stand for 10 min during which time the bright red color obtained on the addition of imidazole faded to orange. Ether (500 mL) precipitated the complex as an oil, which after two triturations with ether was solidified by the addition of isopropyl alcohol. The product was filtered and dried in vacuo. Puri-

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fication was achieved by anion exchange using a column of DEAE-Sephadex A-25 in the NO_3^- form (to remove ClO_4^- and I_3^- ions), evaporating the eluant to dryness and recrystallizing the residue from hot water (5 mL). The orange product was filtered, washed with ethanol and ether, and air-dried. Yield: 0.13 g, 42%.

The IR spectrum ($\nu_{CN} = 2330$ cm^{-1}) was consistent with coordinated nitrile. Anal. Calcd for $[Co(NH_3)_5(NCC(CH_3)_2CO_2C_2H_5)](NO_3)_3$: C, 17.8; H, 5.56; N, 26.8. Found: C, 17.0; H, 5.6; N, 26.8.

$[(NH_3)_5CoNHCOCBr_2CO_2C_2H_5](ClO_4)_2$. Bromine (3 mL) was added dropwise to a stirred ice-cold solution of $[(NH_3)_5CoNCCH_2CO_2C_2H_5](CF_3SO_3)_3$ (17 g) in H_2O (100 mL). With continued cooling of the mixture, a slurry of $NaHCO_3$ (4 g) in H_2O (20 mL) was added in portions over 5 min. The solution was then stirred for 20 min at 20 °C before $HClO_4$ (20 mL, 70%) was added. On cooling of the mixture, a mass of flesh pink crystals formed which were collected and washed with ethanol and ether (yield 11 g). The product was recrystallized from water by cooling and adding $HClO_4$. Anal. Calcd for $[(NH_3)_5CoNHCOCBr_2CO_2C_2H_5](ClO_4)_2$: C, 9.52; H, 3.35; N, 13.32. Found: C, 9.3; H, 3.8; N, 13.2.

$[(NH_3)_5CoNHCOCHBr_2](ClO_4)_2$. NaOH (2 M, 5 mL) was added to a slurry of $[(NH_3)_5CoNHCOCBr_2CO_2C_2H_5](ClO_4)_2$ (1.6 g) in H_2O (15 mL). The solid rapidly dissolved to give an orange solution, and after 15 s the reaction was quenched with $HClO_4$ (12 M, 5 mL). Cooling on ice produced a minor but voluminous amount of orange precipitate which was collected and discarded. It appeared to be a mixture of $[(NH_3)_5CoNHCOCHBr_2]^{2+}$ and $[(NH_3)_5CoNHCOCBr_2COOH]^{2+}$. After 12 h at 20 °C clusters of orange needles had deposited which were collected, washed with ethanol, and dried in vacuo. Anal. Calcd for $[(NH_3)_5CoNHCOCHBr_2](ClO_4)_2$: C, 4.30; H, 3.07; N, 15.04. Found: C, 4.7; H, 3.4; N, 15.2.

$[Co(NH_3)_5(N{\equiv}CCH_2CO_2H)](ClO_4)_3$. $[Co(NH_3)_5OH_2](ClO_4)_3$ (11.6 g) and cyanoacetic acid (8.5 g, 100 mmol) were slurried in water (10 mL) in an evaporating basin, and the mixture was taken to dryness on a steam bath. Water (5 mL) was added to the resultant orange solid, and the mixture was again taken to dryness. The solid residue was cooled, dissolved in water (300 mL), and sorbed on Dowex 50W-X2 resin (200–400 mesh, H^+ form). Elution with 1 M $NaClO_4$ (pH 3) gave two bands, the first red and the second yellow. The separate eluates were reduced in volume on a rotary evaporator until crystallization occurred. After addition of methanol and cooling of the mixture, the product was collected, washed with ethanol and ether, and air-dried. The first band gave rise to pink-orange needles (0.8 g), having $\nu_{CN} = 2260$ cm^{-1} in the infrared spectrum, indicating free C≡N, whence this compound was formulated as $[Co(NH_3)_5(O_2CCH_2CN)](ClO_4)_2$. Anal. Calcd for $CoC_3H_{17}N_6O_{10}Cl_2$: C, 8.44; H, 4.01; N, 19.68; Co, 13.80; Cl, 16.61. Found: C, 8.5; H, 3.9; N, 19.6; Co, 13.9; Cl, 16.5.

The second band resulted in bright yellow flakes (1.5 g, 11%) with $\nu_{CN} = 2325$ cm^{-1}, indicating a coordinated nitrile group; this complex had a visible spectrum $\epsilon_{470} = 68$ and $\epsilon_{336} = 66$ in 0.01 M $HClO_4$ solution. Anal. Calcd for $[Co(NH_3)_5(NCCH_2CO_2H)](ClO_4)_3$: Co, 11.2; C, 6.83; H, 3.44; N, 15.9. Found: Co, 11.3; C, 6.9; H, 3.7; N, 15.7.

$[Co(NH_3)_5(N{\equiv}CCH{=}CH_2)](ClO_4)_3$. $[Co(NH_3)_5N_3](ClO_4)_2$ (10 g) was dissolved in trimethyl phosphate (30 mL) and then diluted with acrylonitrile (~75 mL). Solid $NO(CF_3SO_3)$ was added slowly until all complex had reacted and the resulting mixture left overnight at 40–50 °C. After the mixture was cooled, ether was added to precipitate the complex. It was recrystallized by dissolution in hot water at pH ~3, and the complex was precipitated by the addition of solid $NaClO_4$. The yield was >90%. ^1H NMR (D_2O, ABX spectrum): δ 6.0–7.0 relative to DSS internal reference. Anal. Calcd for $[Co(NH_3)_5(N{\equiv}CCH{=}CH_2)](ClO_4)_3$: Co, 11.9; C, 7.27; H, 3.66; N, 17.0. Found: Co, 11.8; C, 7.4; H, 3.8; N, 16.7.

Kinetics of Base Hydrolysis of $[Co(NH_3)_5(N{\equiv}CCH_2C{\equiv}N)](ClO_4)_3$. A solution of the complex in 1 M $NaClO_4$ (ca. 8×10^{-4} M) was maintained at the desired pH with a pH-stat apparatus and the reaction followed at 397 nm by using a Cary 16 K spectrophotometer at a cell temperature of 25.0 °C. The following Radiometer apparatus was used in the pH-stat assembly: pH meter 26, ABU1 autoburet and TTT1 titrator with a G202B glass electrode and a saturated calomel electrode coupled by a salt bridge containing 1.6 M NH_4NO_3 and 0.2 M $NaNO_3$.

Product Isolation. The resultant solutions from the above kinetic determinations were adjusted to pH 7, diluted, and sorbed on a cation-exchange resin (Dowex 50W-X2, 200–400 mesh, Na^+ form) and the products eluted with 2 M $NaClO_4$. The products of the reaction were Co^{2+}, $[Co(NH_3)_5OH_2]^{3+}$, and $[Co(NH_3)(NHCOCH_2CN)]^{2+}$ measured by atomic absorption spectroscopy.

The amide complex was isolated by evaporation of the above eluant solution but was obtained more simply by the following method. $[Co(NH_3)_5(NCCH_2CN)](ClO_4)_3$ (0.2 g) was dissolved in the minimum quantity of warm water (10 mL, acidified with CH_3COOH) and 1.0 M NaOH solution (4 mL) added. After being left to stand for 90 min, the solution was filtered to remove precipitated cobalt oxides, and the product was crystallized from the filtrate by the addition of solid $NaClO_4$. The pink-yellow solid was filtered, washed with ethanol and ether, and air-dried. Yield: 0.1 g. The complex showed $\nu_{CN} = 2260$ cm^{-1} and $\epsilon_{480} = 74$ and $\epsilon_{345} = 95$ for a solution in 0.01 M NaOH. Anal. Calcd for $[Co(NH_3)_5(NHCOCH_2CN)](ClO_4)_2$: C, 8.46; H, 4.26; N, 23.0. Found: C, 8.5; H, 4.5; H, 22.8.

A yellow protonated form was also isolated by addition of 12 M $HClO_4$ to the solution obtained from the reaction of $[Co(NH_3)_5(NCCH_2CN)]^{3+}$ with OH^-, but as with protonated forms of the complexes $[Co(NH_3)_5(NHCOC_6H_5)]^{2+}$[8] and $[Co(NH_3)_5(NHCOCH_3)]^{2+}$,[6] analytical results indicated incomplete protonation or possibly one proton shared between two of the cations via hydrogen bonding.

Base Hydrolysis of $[Co(NH_3)_5(N{\equiv}CCH{=}CH_2)]^{3+}$ and $[Co(NH_3)_5N{\equiv}CCH_3]^{3+}$. A solution of the complex perchlorate in water ($(0.5–3) \times 10^{-4}$ M) was deaerated with nitrogen and mixed with solutions of deaerated sodium hydroxide solution by using a hand-operated stopped-flow device fitted to a Cary 16K spectrophotometer. The reaction was followed at 260 and 250 nm, respectively, and constant ionic strength of 1.0 ($NaClO_4$). The amide product $[(NH_3)_5CoNHCOCH{=}CH_2]I_2$ was isolated and characterized by microanalysis and ^1H NMR spectroscopy (see paragraph in this section of tracer studies).

Catalysis of Base Hydrolysis of $[Co(NH_3)_5(N{\equiv}CCH{=}CH_2)]^{3+}$ by Carbonate Ion. In a similar method to the base hydrolysis studies above, solutions of the complex were mixed with carbonate/bicarbonate buffers of varying total carbonate concentrations (pH maintained at ca. 9.6) by using the hand-operated stopped-flow device. Ionic strength was maintained at 1.0 ($NaClO_4$), $T = 25.0$ °C, and all runs were followed at $\lambda = 260$ nm by using a Cary 16K spectrophotometer.

Tracer Studies of CO_3^{2-} Reaction with $[Co(NH_3)_5(N{\equiv}CCH{=}CH_2)]^{3+}$. A sample of anhydrous Na_2CO_3 (2 g) was enriched by allowing a solution in $H_2{}^{18}O$ (ca. 1.5 atom %) to stand for 14 days at 25 °C: the $H_2{}^{18}O$ was evaporated and the $Na_2C^{18}O_3$ dried for 2 h at 260 °C and then kept in an evacuated desiccator.

$Na_2C^{18}O_3$ (0.50 g) was dissolved in $H_2{}^{16}O$ (CO_2 free; 3 mL): immediately, yellow $[Co(NH_3)_5(N{\equiv}CCH{=}CH_2)](ClO_4)_3$ (0.30 g) suspended in $H_2{}^{16}O$ (2 mL) was added, whereupon the complex dissolved and the solution became pink. Excess NaI was added after a fixed period (1, 5, and 7 min) to crystallize anhydrous $[Co(NH_3)_5(NHCOCH{=}CH_2)]I_2$. The complex was washed thrice with cold 1 M NaI solution and then several times with methanol and dried overnight in vacuo over P_2O_5. Half of the solid was recrystallized from water (ca. 2 mL) containing 1 drop of glacial acetic acid. ^1H NMR (D_2O, ABX spectrum): δ 5.2–6.6 relative to DSS internal reference. Anal. Calcd for $[(Co(NH_3)_5(NHCOCH{=}CH_2)]I_2$: C, 7.70; H, 4.09; N, 18.0; Co, 12.6; I, 54.2. Found: C, 7.9; H, 4.0; N, 17.9; Co, 12.7; I, 54.1.

The analysis of the enrichment in the acrylamide product was achieved by using the Anbar and Guttman method.[9] $[Co(NH_3)_5(NHCOCH{=}CH_2)]I_2$ (0.1 g) was mixed with $HgCl_2{\cdot}Hg(CN)_2$ and heated at 400 °C for 15 h in a break-seal tube. The CO_2, separated from the other gases in a gas chromatograph, was collected by using He as the carrier gas and the ^{18}O content analyzed by using an Atlas M-86 mass spectrometer, as outlined previously.[9] The enrichment in CO_3^{2-} was determined by adding acid to the solid sample in a stream of He and trapping the CO_2 produced. In one experiment, the reaction mixture was also treated in this way to sample the enrichment of reacted CO_3^{2-}.

pK_a Determination. The pK_a values for $[Co(NH_3)_5(N{\equiv}CCH_2C{\equiv}N)]^{3+}$ and $[Co(NH_3)_5(N{\equiv}CCH_2CO_2C_2H_5)]^{3+}$ were determined by the following method. A solution (ca. 8×10^{-4} M) of the complex as the perchlorate salt in 1 M $NaClO_4$ (pH ca. 3) was mixed with equal volumes of various buffer solutions ([buffer] = 0.2 M; $\mu = 1.0$, $NaClO_4$) by using a stopped-flow apparatus. The subsequent reaction was followed for ca. 3 min at a fixed wavelength ($\lambda = 397$ nm for $[Co(NH_3)_5(NCCH_2CN)]^{3+}$, $\lambda = 527$ nm for $[Co(NH_3)_5(NCCH_2CO_2C_2H_5)]^{3+}$) by using a Cary 16K spectrophotometer at a cell temperature of 25.0 °C. The pH of each solution was measured with a Radiometer 26 pH meter. In each case, the curve was extrapolated to give the optical density at the instant of mixing and the pK_a evaluated.[10]

Polymerization Studies. Acrylonitrile, methacrylonitrile, and dimethylformamide (DMF) were purified and distilled before use.[11] Styrene, methyl methacrylate, and pyridine were dried and distilled be-

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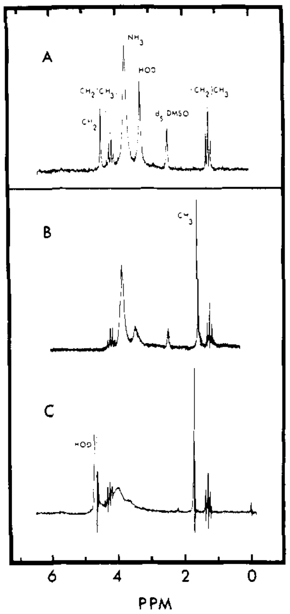

Figure 1. 100-MHz ^{1}H NMR spectra of $[Co(NH_3)_5(NCCH_2CO_2C_2H_5)]^{3+}$ in Me_2SO-d_6 solution (A) and of $[Co(NH_3)_5(NCC(CH_3)_2CO_2C_2H_5)]^{3+}$ in Me_2SO-d_6 solution (B) and in acidified D_2O solution (C) (sodium 4,4-dimethyl-4-silapentanesulfonate, internal reference, DSS).

fore use. All polymerizations were carried out in an all-glass vacuum line by using the following procedure. Dried and deaerated DMF (ca. 10 mL) was distilled into a 50-mL flask containing a magnetic stirrer bar and the desired complex (ca. 0.02 g). The monomer (ca. 2 mL) was then distilled into the flask, followed by pyridine (ca. 0.1 mL) if required. The flask was sealed off from the line; the contents were melted, mixed, and left for 48 h protected from the light. Subsequently, the solvent was removed and the resultant polymer recrystallized (twice) by dissolution in DMF and precipitation by the slow addition of water. The product was dried in vacuo for 3 days. The ^{1}H NMR spectra of samples of polymethacrylonitrile (PMAN) were measured by using a Varian HA-100 spectrometer and a 7% solution in CD_3NO_2 at 90 °C with hexamethyldisiloxane as an internal reference,[12] and trimethyl phosphate as an internal lock. The polystyrene–polymethyl methacrylate copolymer was not soluble in CD_3NO_2, and its ^{1}H NMR spectrum was measured in C_6D_6 solution (7%) by using a JEOL MH-100 spectrometer with tetramethylsilane as internal reference at 34 °C.

Results and Discussion

The pentaamminecobalt(III) complexes of three nitriles, malononitrile ($NC-CH_2-CN$), ethyl cyanoacetate ($NC-CH_2-CO_2C_2H_5$), and cyanoacetic acid ($NC-CH_2-CO_2H$), have been isolated and characterized analytically and spectrally. The IR spectra of the complexes all showed an absorption in the range 2315–2330 cm^{-1} attributed to the $-C\equiv N$ stretching mode for the coordinated nitrile group.[4,13,14] In addition, coordinated malononitrile gave an absorption at 2260 cm^{-1}, appropriate to ν_{CN} for uncoordinated nitriles (ca. 2275 cm^{-1})[15] as did the $[(NH_3)_2CoOOCCH_2CN]^{2+}$ ion.

The ^{1}H NMR spectrum of $[Co(NH_3)_5(NCCH_2CO_2C_2H_5)]^{3+}$ in Me_2SO-d_6 is shown in Figure 1A. The complexes of malononitrile and cyanoacetic acid were found to have limited stability in Me_2SO, with the solvent replacing the nitrile in the coordination sphere over a period of hours at 20 °C. In all three cases, the ^{1}H NMR spectra measured in D^+/D_2O mixture indicated a rapid exchange of the methylene protons.

Acidified aqueous solutions of these complexes varied considerably in stability, the ethyl cyanoacetate complex being the most stable. Both the cyanoacetic acid and malononitrile complexes underwent an initial reaction, identified as hydrolysis of the coordinated nitrile group for $[Co(NH_3)_5(NCCH_2CN)]^{3+}$ ($k_{obsd} = 9.6 \times 10^{-5}$ s^{-1}; pH 3.0, $\mu = 1.0$, 25 °C), followed by a slower substitution of the coordinated amide by water.

Table I. Base Hydrolysis of $[Co(NH_3)_5(N{\equiv}CCH{=}CH_2)]^{3+\,a}$

$[OH^-]$	k_{obsd}, s^{-1}	$k_{OH} = k_{obsd}/[OH^-]$, M^{-1} s^{-1}
0.0010	3.49×10^{-2}	34.9
0.0025	8.49×10^{-2}	34.0
0.0050	1.67×10^{-1}	33.3
0.010	3.67×10^{-1}	36.7
0.010	3.70×10^{-1}	37.0
		$k_{OH}^{av} = 35.2$

[a] $[Co] = 6.70 \times 10^{-5}$ M; $\mu = 1.0$ ($NaClO_4$); $T = 25.0$ °C; $\lambda = 270$ nm; all solutions deaerated.

The addition of base to solutions of the three yellow nitrile complexes resulted in the immediate formation of deep red solutions. These changed slowly to yellow solutions which differed spectrally from the initial nitrile species. The initial rapid reaction is reversible on adding acid and is attributed to the deprotonation of the acidic methylene protons. For uncoordinated malononitrile the pK_a of the methylene protons is 11.3.[16] On coordination, this value falls to 5.7 ± 0.1 (0.1 M pyridine/$HClO_4$ buffer, $\mu = 1.0$ ($NaClO_4$), 25.0 °C). Similarly for ethyl cyanoacetate, the pK_a[16] is reduced on coordination from >9 to 7.58 (0.1 M "Tris"/$HClO_4$ buffer, $\mu = 1.0$ ($NaClO_4$), 25.0 °C). The deprotonated complexes are presumably stabilized by extensive delocalization of the negative charge throughout the coordinated ligand. A consequence of this is the intense absorption which develops in the first ligand field band on deprotonation: the maximum molar absorptivity $\epsilon_{532} = 450$ M^{-1} cm^{-1} for $[Co(NH_3)_5(NCCHCN)]^{2+}$ is to be compared with $\epsilon_{474} = 72$ M^{-1} cm^{-1} for the protonated form. The former intensity is more consistent with a substantial contribution from ligand-to-metal charge transfer whereas the latter intensity is consistent with ligand field absorption and is typical in complexes of this type. A similar result was observed for the ethyl cyanoacetate complex where the deprotonated complex ($\epsilon_{527}^{max} = 550$ M^{-1} cm^{-1}) absorbs much more strongly than the parent ion ($\epsilon_{465}^{max} = 64$ M^{-1} cm^{-1}).

The subsequent decay of the deprotonated complex was unusually rapid for coordinated cyanoacetic acid and produced predominantly Co(II). For the other two complexes, the decay of the red solution was slower and gave both Co(II) and hydrolysis of the coordinated nitrile. Three interesting aspects arise from these properties: the mechanism of the base-hydrolysis process, the reactions of the coordinated carbanion, and the electron-transfer process from the deprotonated ligand resulting in the reduction of Co(III) to Co(II) and a ligand radical.

Base hydrolysis of coordinated nitrile in $[Co(NH_3)_5(NCR)]^{3+}$ ions has been attributed to direct attack of OH^- at the nitrile carbon atom.[4,6] For $[(NH_3)_5CoN{\equiv}CC_6H_5]^{3+}$, this seems the only feasible explanation[4] for the first-order dependence on $[OH^-]$. Although C-proton exchange occurs with coordinated CH_3CN faster than amide formation,[6] no exchange was observed on the aromatic ring of coordinated NCC_6H_5. Also, it does not seem likely that deprotonation of the ammine centers would lead to amide formation. The results for hydrolysis of $[Co(NH_3)_5NCCH{=}CH_2]^{3+}$ also support this proposal (Table I). The linear pseudo-first-order plots of log $(A_t - A_\infty)$ vs. time obtained over at least $3t_{1/2}$ demonstrate a first-order dependence of the rate on $[OH^-]$ for the production of coordinated acrylamide. Clearly OH^- adds at the nitrile carbon atom and not at the olefin β-carbon atom nor is there any proton exchange at the olefin moiety. Similar results are obtained in the presence of the CO_3^{2-} ion which also generates the acrylamide complex.

One striking feature of this study was the remarkable dependence of the base-hydrolysis rate on CO_3^{2-} concentration. The hydrolysis reaction was therefore studied at 25 °C by using carbonate/bicarbonate buffer mixtures, and the results are sum-

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Table II. Catalysis of Base Hydrolysis of $[Co(NH_3)_5(N{\equiv}CCH{=}CH_2)]^{3+}$ by CO_3^{2-} [a]

pH	$10^3k'_{OH}$,[b] s^{-1}	k_{obsd}, s^{-1}	$(k_{obsd} - k'_{OH})/[CO_3^{2-}]$, M^{-1} s^{-1}	$[carbonate]_T$, M	$[CO_3^{2-}]$,[c] M
9.64	2.59	2.78×10^{-2}	1.0	0.0455	0.0245
9.67	2.78	6.69×10^{-2}	1.0	0.1138	0.0634
9.59	2.31	7.85×10^{-2}	0.9	0.1667	0.0853
9.71	3.05	1.41×10^{-1}	1.0	0.2275	0.1319

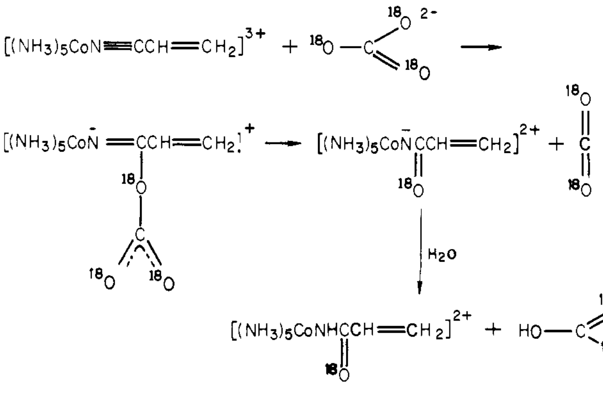
[a] [Co] = 6.70×10^{-5} M; T = 25 °C; $\mu = 1.0$ ($NaClO_4$); λ = 270 nm. [b] Assuming $k_{OH} = 35.2$ M^{-1} s^{-1} (from Table I); $pK_w = 13.77$.[19] [c] Assuming $pK_a = 9.57$ for $HCO_3^{2-} \rightleftarrows CO_3^{2-} + H^+$ at $\mu = 1.0$.[19]

Table III. Hydrolysis of $[(NH_3)_5CoN{\equiv}CCH{=}CH_2](ClO_4)_3$ (0.12 M) with $Na_2C^{18}O_3$ (1 M) in $H_2{}^{16}O$ at 25 °C

reaction time, min	species	^{18}O label,[a] atom %	enrichment	% ^{18}O content in amide
1	CO_3^{2-}	1.4087	1.2071	
	amide[c]	1.1073	0.9057	75
5	CO_3^{2-}	1.4086	1.2070	
	amide	0.7402	0.5386	45
7	CO_3^{2-}	1.4088	1.2072	
	amide	0.5993	0.3977	33
	CO_3^{2-} [d]	1.3546	1.1530	95.5

[a] Obtained from the ion current ratios (R) using relationships atom % = $R/(2 + R)$. [b] Atom percent levels minus the normal $C^{18}O_2$ content 0.2016 atom %. [c] $[(NH_3)_5CoNHCOCH{=}CH_2]I_2$. [d] CO_2 from CO_3^{2-} in the reaction mixture.

Scheme I



Scheme II

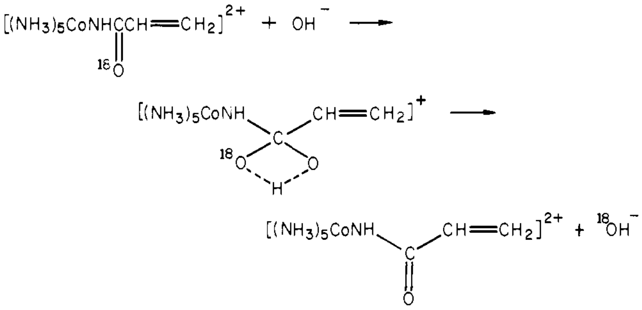


Table IV. Rates of Base Hydrolysis of $[Co(NH_3)_5NCCH_3](ClO_4)_3$ in 0.01 M NaOH[a]

temp, °C	k_{OH}, M^{-1} s^{-1}	temp, °C	k_{OH}, M^{-1} s^{-1}
15.2	0.945	35.3	8.15
24.1	2.36	40.0	12.6
30.8	4.62		

$E_a = 18.8 \pm 1.0$ kcal mol^{-1}
$\Delta S^{\ddagger} = +4.4$ cal deg^{-1} mol^{-1}

[a] [complex] = 2.5×10^{-4} M; λ = 250 nm; $\mu = 1.0$ ($NaClO_4$).

marized in Table II. . The data obey the rate law $k_{obsd} = k_{OH^-}[OH^-] + k_c[CO_3^{2-}]$ with $k_{OH} = 35$ M^{-1} s^{-1} and $k_c = 1.0$ M^{-1} s^{-1}: the carbonate ion being only a factor of 35 less efficient than OH^- in effecting hydrolysis. A question immediately arises concerning the mechanism of involvement of CO_3^{2-}. Is it by a nucleophilic mechanism or by a general-base process? The determination can be made by using ^{18}O tracer studies, since in the pH region for which the measurements shown in Table II are made, CO_3^{2-} exchanges slowly with the oxygen atoms in solvent water (for example, in 0.02 M Na_2CO_3, $t_{1/2}$ for exchange is ca. 28 h).[17] The tracer experiment was carried out by dissolving the complex in a solution of 1 M $Na_2C^{18}O_3$ of known enrichment in normal water. In different experiments, the amide product was precipitated after different intervals (1, 5, and 7 min) as the anhydrous iodide salt. (The rate constant for hydrolysis of $[Co(NH_3)_5(N{\equiv}CCH{=}CH_2)](ClO_4)_3$ in 0.25 M Na_2CO_3 is 0.28 s^{-1} at 25 °C, so hydrolysis was complete before the complex was precipitated.)

The results of the tracer experiment are given in Table III. Extrapolation of enrichment to the time required for completion of the hydrolysis process reveals that the initial product contains ca. 90% enrichment, indicating that CO_3^{2-} is involved in direct nucleophilic attack on the nitrile carbon atom, yielding an oxygen atom to the coordinated amide. The observed discrepancy from 100% enrichment in this experiment is due to concomitant hydrolysis of the nitrile by unlabeled OH^-.[18] The tracer experiments also show that the carbonate ion in the final reaction mixture is diluted in label by 4.5% compared with the expected dilution of 4.2%. The proposed mechanistic scheme for hydrolysis of coordinated acrylonitrile by CO_3^{2-} is shown (Scheme I).

Carbonate ion attacks the nitrile C atom, and either CO_2 is eliminated or a water molecule takes CO_2 off the complex as H_2CO_3. If the latter path obtained, it could be expected that this would also be a route to exchange of CO_3^{2-} oxygen atoms with solvent and that was not observed. A preference therefore exists for the path involving decarboxylation of the carbonate ester. Subsequently, protonation of the amide N generates the acrylamide complex.

A complicating feature in the reaction should be ion pairing between the parent 3^+ ion and the CO_3^{2-} anion. Analogous association constants[21] for $[Co(NH_3)_5OH_2]^{3+}$ and SO_4^{2-} are in the vicinity of $\sim 10^3$ M^{-1}. If this value holds for the present case, then all the parent complex should be ion paired and the rate law more properly formulated as $-d(CoNCR)/dt = k[(NH_3)_5CoN{\equiv}CR^{3+}{\cdot}CO_3^{2-}][Co_3^{2-}]$. A dependence of the rate of hydrolysis of coordinated nitriles on carbonate ion has been reported previously for Ru(III) and Rh(III) complexes,[20] although no direct tracer evidence was presented to distinguish between the nucleophilic and general-base mechanism. However, the involvement of CO_3^{2-} in the hydrolysis of uncoordinated nitriles does not appear to have been observed.

When these reactions were carried out for longer periods, a subsequent slower exchange process occurred with solvent water resulting in the loss of ^{18}O label from the coordinated amide (Table

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(18) A solution of 1 M Na_2CO_3 has a pH of $\sim$11.8. With the assumption of $pK_w = 14.17$ for a solution of $\mu = 3.0$ at 25 °C,[19] $[OH^-] = 4 \times 10^{-3}$ M. Consequently, under the conditions of the experiment, $k'_{OH} = k_{OH}[OH^-] = 0.14$ s^{-1} and $k'_c = k_c[CO_3^{2-}] = 1.0$ s^{-1} whence $\sim$14% hydrolysis of the nitrile by unlabeled OH^- would be expected.

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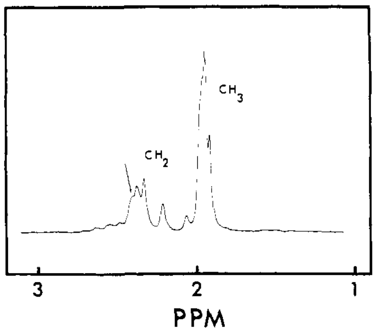


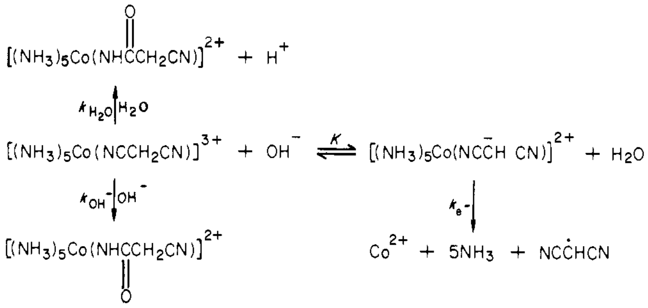
Figure 2. 100-MHz ^1H NMR spectrum of polymethacrylonitrile (7% in CD_3NO_2, 90 °C, hexamethyldisiloxane, internal standard).

III). In 1 M Na_2CO_3 solution, the concentrations of bicarbonate ion and carbon dioxide are low ($[HCO_3^-] \approx 6 \times 10^{-3}$ M; $[CO_2] \approx 6 \times 10^{-7}$ M)[22] so that it is unlikely that either of these species is involved in the exchange process. Neither does CO_3^{2-} lead to direct exchange, because its own exchange rate with the solvent[17] is much slower than the observed rate of amide exchange. Consequently, the most reasonable path for the loss of label from the amide would be by OH^- addition or general-base (CO_3^{2-}) catalyzed water addition, and a possible mechanism is presented in Scheme II although this exchange process has not been investigated in detail.

The base hydrolysis of $[Co(NH_3)_5(NCCH_3)]^{3+}$ has been studied at 25 °C and $\mu = 1.0$.[6] It was of interest to compare the activation parameters of the coordinated acetonitrile to those of the free ligand, and the rates were measured at five different temperatures (Table IV). From the data, the following activation parameters were calculated: $E_a = 18.8 \pm 1.0$ kcal/mol and $\Delta S^\ddagger = +4$ cal/(deg mol). The corresponding data for free acetonitrile[23] are $E_a = 19.1$ kcal/mol and $\Delta S^\ddagger = -23$ cal deg^{-1} mol^{-1}, showing that the difference in rate is reflected in the $\Delta S^\ddagger$ term while E_a is unchanged for the two reactions. Essentially the same results were observed for $[Co(NH_3)_5(NCC_6H_5)]^{3+}$ and free benzonitrile:[4] here, for the complex $E_a = 16.5$ kcal/mol and $\Delta S^\ddagger = +2.7$ cal deg^{-1} mol^{-1} compared with $E_a = 19.9$ kcal/mol and $\Delta S^\ddagger = -15.2$ cal deg^{-1} mol^{-1} for benzonitrile (in 50% acetone). The change in $\Delta S^\ddagger$ for the hydrolysis reactions from highly negative for the free nitriles to slightly positive for the coordinated nitriles may simply reflect the 3+ charge on the latter species.[24] However, it appears to be a characteristic of the coordinated ligand reactions, and there is as yet no clear correlation between charge neutralization and rate enhancement for reactions of this type.

The hydrolysis process was studied throughout the pH range 1–12 for the malononitrile complex. Continuous scans of the electronic spectra during these reactions indicated that the process was not simple. Some $[Co(NH_3)_5OH_2]^{3+}$ was detected in the reaction mixtures arising from a subsequent loss of the amide ligand. However, linear plots of log $(A_t - A_\infty)$ against time were observed for at least $3t_{1/2}$, indicating pseudo-first-order kinetics for the production of the amide and Co^{2+}. In 1 M $HClO_4$ 1% Co^{2+} was produced while the amount increased to 25% at $7 < pH < 10$. A reaction profile of the observed rate with pH for the malononitrile species is shown in Figure 2. The data and observations are consistent with Scheme III. The derived value for K (implying $pK_a \approx 5.3$) is consistent with the independently measured pK_a value of 5.7 ± 0.1 for the malononitrile complex.

Scheme III



$$k_{obsd} = \frac{k_{H_2O} + k_{OH}[OH^-] + k_{e^-}K[OH^-]}{1 + K[OH^-]}$$

$$k_{H_2O} = 1.0 \times 10^{-4}\ s^{-1}$$
$$k_{OH} = 5 \times 10^5\ M^{-1}\ s^{-1}$$
$$k_{e^-} = 3.5 \times 10^{-4}\ s^{-1}$$
$$K = 5.2 \times 10^8\ M^{-1}$$

The three paths are competitive but in the acid region nucleophilic attack of OH_2 at the nitrile C atom dominates the kinetics. Only ~1% Co^{2+} was produced under these conditions. However above the pK_a for coordinated malononitrile the reduction path is more dominant (25%). Presumably a unimolecular intramolecular electron transfer from the generated carbanion to the cobalt(III) ion accounts for this path ($k_{e^-} = 3.5 \times 10^{-4}\ s^{-1}$). Concomitantly, the nitrile complex hydrolyzes to the amide. Either, H_2O could react with the protonated nitrile or OH^- could attack the nitrile C atom of the protonated ligand. We have argued the mechanism by the latter path primarily because it appears to be the effective route for the CH_3CN, C_6H_5CN, and $CH_2{=}CHCN$ ligands.

The hydrolysis of coordinated malononitrile takes place under much milder conditions than the base hydrolysis of malononitrile to malonamide ($NaOH$/liquid NH_3 at 125 °C for 6 h).[25] Furthermore, the hydrolysis is specifically confined to one nitrile group.

Reactions of the Deprotonated Ligand. Malononitrile is a very reactive compound because of its acidic methylene group and two cyano functions and finds considerable use in industrial chemistry, particularly in the production of heterocyclic compounds.[26] The enhancement of acidity of these methylene protons on coordination means that the carbanion can be produced under milder conditions than those used for the uncoordinated case (NaH/Me_2SO or $NaOEt/EtOH$).[26]

For the complexes of malononitrile and ethyl cyanoacetate it was found that the addition of the substrates methyl iodide, acetone, formaldehyde, tosyl chloride, and methyl pyruvate to basified solutions (either in water or Me_2SO) led to a rapid decrease in the intensity of the color of the solution, indicating substitution at the methylene group. Bromine also rapidly reduced the color and produced $[(NH_3)_5CoNHCOCBr_2CO_2C_2H_5]^{2+}$. Bromination of the carbanion is clearly faster than hydrolysis, but the amide product is observed because the dibromo ester nitrile is very reactive and hydrolyzes as soon as it is formed. It is also worth noting that the dibromocyanoacetic ester complex hydrolyzes and decarboxylates in base to $[(NH_3)_5CoNHCOCHBr_2]^{2+}$.

For confirmation of the nucleophilic reaction of the stabilized carbanion, the product of the reaction of $[Co(NH_3)_5(NCCH_2CO_2C_2H_5)]^{3+}$ with excess MeI in Me_2SO (using imidazole as base) was isolated as $[Co(NH_3)_5(NCC(CH_3)_2CO_2C_2H_5)]^{3+}$. That the nitrile and ester moieties remained intact was shown by the IR spectrum. The ^1H NMR spectra in Me_2SO-d_6 (Figure 1B) and acidified D_2O (Figure 1C) indicated a single methyl resonance which integrated to give a 2:1 ratio with the CH_3 triplet of the ethyl ester group, thereby proving disubstitution. Experiments performed by using a deficiency of MeI showed only the disubstituted products, indicating that the second substitution reaction is more rapid than the first. The product also hydrolyzed in OH^- solutions with a similar rate constant (2.2 $M^{-1}\ s^{-1}$ at 25 °C) to that of the acetonitrile complex ($k_{OH} = 3.40\ M^{-1}\ s^{-1}$).[6] The products of the other reactions at the carbanion

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[22] These values are calculated using the following equilibrium constants ($\mu = 3.0$, 25 °C):[19] $HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$, $pK_a = 9.56$; $CO_2 + CO_3^{2-} + H_2O \rightleftharpoons 2HCO_3^-$, log $K = 2.53$.

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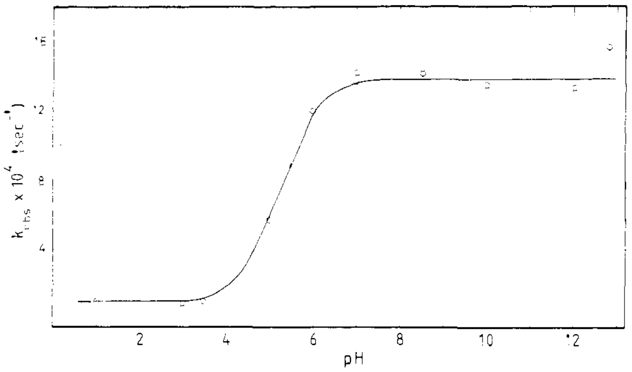

Figure 3. Reaction profile for pH dependence of observed pseudo-first-order rate constants for hydrolysis of $[Co(NH_3)_5(NCCH_2CN)]^{3+}$ (μ = 1.0 ($NaClO_4$); 25 °C).

were not isolated, but clearly the carbanion is very reactive toward these reagents and coordination of the nitrile allows the chemistry to be done in a regiospecific manner. The nitrile may be hydrolyzed without affecting the ester, and the carbanion may be alkylated without affecting the nitrile or the ester.

Polymerization Studies. Subsequent to deprotonation of the methylene proton in the $[Co(NH_3)_5(NCCH_2X)]^{3+}$ species, there is some reduction of the metal ion to Co(II) concomitant with the hydrolysis of the coordinated nitrile which increases in the order X = $CO_2C_2H_5 < CN < CO_2^-$. The reduction is enhanced at high pH. This reduction occurs by electron transfer to the metal from the delocalized carbanion and results in an organic radical, i.e.

$$(NH_3)_5Co^{3+}N{\equiv}CCH_2X \xrightarrow{OH^-} [(NH_3)_5CoN{\equiv}C\dot{C}HX]^{2+} \rightarrow \text{“}(NH_3)_5Co^{2+}\text{”} + N{\equiv}C\dot{C}HX$$

Whether the radical remains bound to the Co(II) ion is not certain.

Such an electron transfer producing a radical organic species has been reported previously[27] for the $[Co(NH_3)_5(N{\equiv}CCH_2C_6H_5)]^{3+}$ ion, which even on dissolution in neutral H_2O yields the corresponding carbanion and then stilbene dinitrile $C_6H_5CH(CN)CH(CN)C_6H_5$ in >90% yield.

When acrylonitrile was added to the aqueous solution in which basification was carried out for the cyanoacetic acid complex, white polyacrylonitrile precipitated out. Such an observation is not new and has previously been used as evidence for free radicals in the elucidation of mechanisms of electron-transfer reactions.[28,29] However it was decided to investigate the stereochemistry of the polymers produced by using the three complexes as initiators, because the varying lifetimes of their carbanions might lead to alternate forms of polymerization initiation.

In DMF solution, the three complexes were found to initiate the polymerization of acrylonitrile and methacrylonitrile whether or not base was added. ^1H NMR studies in CD_3NO_2 solutions of the polymethacrylonitrile (PMAN) samples obtained revealed the polymers to be identical regardless of the complex or the presence of base. Further, by comparison of these spectra with those obtained for conventional radical (azobis(isobutyronitrile), AIBN) and anionic (diethylmagnesium, $MgEt_2$) initiation of methacrylonitrile polymerization,[12] it was found that the polymers had some greater degree of isotacticity than anticipated for radical polymerization. Figure 3 shows the ^1H NMR spectrum of PMAN initiated by $[Co(NH_3)_5(NCCH_2CO_2C_2H_5)]^{3+}$, and the presence of the shoulder (arrowed) on the high-field side of the methylene signal indicates some isotacticity.[12]

A copolymerization of styrene and methyl methacrylate was thus undertaken to ascertain the mode of initiation. ^1H NMR studies of a polymer obtained by using $[Co(NH_3)_5(NCCH_2CO_2C_2H_5)]^{3+}$ as initiator revealed a 50/50 copolymer, consistent with a radical process (anionic initiation would have led to polymethyl methacrylate (PMMA) alone and cationic polymerization to polystyrene alone).[30,31] DMF is not an ideal solvent to initiate anionic polymerization (due to the availability of protons), and the carbanions generated from the complexes do not appear capable of transferring the charge to the monomers. However, the mildness of conditions for the radical polymerization and the ease of removal of the byproduct (Co^{II}) make these complexes potentially useful as radical initiators.

One interesting feature of the $[Co(NH_3)_5NCCH_2COOH]^{3+}$ ion is the prospect of inducing the radical path by varying the concentration of deprotonating base. The base concentration should govern the concentration of the carbanion produced, and thence the electron-transfer rate will control the production of radicals. Preliminary indications are that the radicals could be produced in a large burst at high base concentrations and relatively slowly over a long period at low base concentrations. In this way, the chain length of the polymer produced might be controlled.

Acknowledgment. We wish to thank the Microanalytical Service of the Australian National University and A. J. Herlt for assistance with the kinetics and equilibrium measurements.

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