

## Reactions of Nitriles Bound to Cobalt(III) Amines

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Dedicated to Jannik Bjerrum on the occasion of his 70th birthday

Rapid intramolecular oxidation of the carbanions  $[\text{Co}(\text{NH}_3)_5\text{NC}\bar{\text{C}}\text{HR}]^{2+}$  ( $\text{R} = \text{C}_6\text{H}_5$ ,  $\text{CH}=\text{CH}_2$ ) generated by rapid  $\text{H}^+$  loss from  $[\text{Co}(\text{NH}_3)_5\text{-NCCH}_2\text{R}]^{3+}$  yields the nitrile radicals which immediately dimerize. Reduction of coordinated nitriles with  $\text{BH}_4^-$  and Michael additions of carbanions and  $\text{PO}_4^{3-}$  to coordinated acrylonitrile occur more than  $10^4$ -fold faster than the same reactions for the uncoordinated nitriles. Attack of  $\text{CN}^-$  at the nitrile C atom of  $(\text{NH}_3)_5\text{CoN}\equiv\text{CCH}_3^{3+}$  followed by intramolecular condensations yields a tridentate bis(amidine) amino methyl malonate chelate.

When nitriles are coordinated to a metal ion a considerable increase in their reactivity has been observed for several types of reactions.<sup>1–13</sup> The rate of attack of  $\text{HO}^-$  at the nitrile carbon atom is enhanced by a factor of  $10^6$ – $10^8$  when the nitrile is attached to the  $\text{M}(\text{NH}_3)_5^{3+}$  moiety ( $\text{M} = \text{Co}, \text{Rh}, \text{Ru}$ ) resulting in the corresponding N-bound amide complex. Furthermore the  $\text{Co}(\text{NH}_3)_5^{3+}$  fragment enhances the activity of the  $\alpha$  methylene group by *ca.*  $10^6$ . Using nitriles with sufficiently labile methylene groups such as  $\text{NCCH}_2\text{CN}$ ,  $\text{NCCH}_2\text{-CO}_2\text{C}_2\text{H}_5$  and  $\text{NCCH}_2\text{CO}_2\text{H}$  it was possible to generate the  $\text{Co}(\text{NH}_3)_5\text{NC}\bar{\text{C}}\text{HR}^{2+}$  carbanions in aqueous solution by adding base.<sup>10</sup> The carbanions subsequently decayed by losing an electron to the cobalt(III) centre. They were also found to undergo nucleophilic reactions with added substrates such as methyl iodide, formaldehyde, tolyl chloride and

pyruvic acid. The product of the reaction of  $[\text{Co}(\text{NH}_3)_5\text{NCCH}_2\text{CO}_2\text{C}_2\text{H}_5]^{3+}$  with excess  $\text{CH}_3\text{I}$  in the presence of base in  $(\text{CH}_3)_2\text{SO}$  was characterized as the disubstituted  $[\text{Co}(\text{NH}_3)_5\text{NCC}(\text{CH}_3)_2\text{-CO}_2\text{C}_2\text{H}_5]^{3+}$  complex. The reduction of the metal ion to cobalt(II) takes place by electron transfer from the carbanion to the metal resulting in a nitrile radical which triggered the polymerisation of acrylonitrile added to the reaction mixture. The results were sufficiently interesting to prompt further exploration into the reactivity of coordinated nitriles, the production and reactions of nitrile radicals, other possible reactions induced by activation from the metal ion and the distance over which such an activation might extend. This paper reports the rapid production and reactions of the coordinated organic radicals  $\text{PhCHCN}$  and  $\text{NCCHCH}=\text{CH}_2$ , the reduction of coordinated nitriles by  $\text{BH}_4^-$  in aqueous solution, the cyanoethylation reactions of  $[\text{Co}(\text{NH}_3)_5\text{NCCH}=\text{CH}_2]^{3+}$  with acetyl acetone, nitromethane, malononitrile and phosphate ion and nucleophilic addition of cyanide ion to the coordinated nitrile carbon atom.

### EXPERIMENTAL

All chemicals were analytical grade.  $^1\text{H}$  NMR spectra were recorded on a JEOL 100 MHz Minimar spectrometer. Cary 14 and 118C spectrophotometers were used for the kinetics and IR spectra were recorded using a Perkin-Elmer PE 225 spectrometer using KBr discs. The mass spectra were recorded on an AEI MS 902 spectrometer.

The nitrile complexes  $[\text{Co}(\text{NH}_3)_5\text{N}\equiv\text{CR}](\text{ClO}_4)_3$  were generally prepared either by dissolving  $[\text{Co}(\text{NH}_3)_5\text{TMP}](\text{ClO}_4)_3$ , (TMP = trimethylphos-

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phate), in the appropriate nitrile<sup>14</sup> and leaving the mixture at 40 °C for ~24 h or by treating [Co(NH<sub>3</sub>)<sub>5</sub>N<sub>3</sub>](ClO<sub>4</sub>)<sub>2</sub> with NO(CF<sub>3</sub>SO<sub>3</sub>) using the appropriate nitrile as the solvent and leaving the resulting mixture at 40 °C for ~24 h or until it turned yellow. Where the complexes were not soluble in the nitriles a small amount of TMP was added to effect dissolution. The nitrile complexes were isolated from the reaction mixtures upon precipitation with ether. They were recrystallized by dissolving in water (40–50 °C, pH ~4) followed by the addition of NaClO<sub>4</sub> or HClO<sub>4</sub>. Care was taken to keep the reaction mixtures containing the NCCH<sub>2</sub>C<sub>6</sub>H<sub>5</sub> and NCCH<sub>2</sub>CH=CH<sub>2</sub> complexes acidic by the addition of a few drops of concentrated H<sub>2</sub>SO<sub>4</sub> and the complexes were recrystallized from 0.1 M HClO<sub>4</sub>. For [Co(NH<sub>3</sub>)<sub>5</sub>NCCH<sub>2</sub>NHCOCH<sub>3</sub>](ClO<sub>4</sub>)<sub>3</sub> where the free nitrile is a solid the complex was prepared by mixing [Co(NH<sub>3</sub>)<sub>5</sub>TMP](ClO<sub>4</sub>)<sub>3</sub> (1 g) with the nitrile (2 g) and heating on a steam bath until the melt turned orange. The mixture was cooled and extracted several times with CHCl<sub>3</sub> to remove excess nitrile. The product was dissolved in water and sorbed on a cation exchange column (SP-Sephadex C-25) and eluted with 0.3 M NaClO<sub>4</sub> at pH ~4. The eluent containing the main yellow band was collected and taken down to a small volume on a vacuum evaporator. The yellow crystalline product was filtered off, washed with ethanol and ether and recrystallized as above. Anal. [Co(NH<sub>3</sub>)<sub>5</sub>NCCH<sub>2</sub>NHCOCH<sub>3</sub>](ClO<sub>4</sub>)<sub>3</sub>·H<sub>2</sub>O (CoN<sub>7</sub>H<sub>23</sub>C<sub>4</sub>Cl<sub>3</sub>O<sub>14</sub>): C, H, N. IR: 2330 (w) cm<sup>-1</sup>. Anal. [Co(NH<sub>3</sub>)<sub>5</sub>NCCH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>](ClO<sub>4</sub>)<sub>3</sub>(CoN<sub>6</sub>C<sub>8</sub>H<sub>22</sub>Cl<sub>3</sub>O<sub>12</sub>): C, H, N. Anal. [Co(NH<sub>3</sub>)<sub>5</sub>NCCH<sub>2</sub>CH=CH<sub>2</sub>](ClO<sub>4</sub>)<sub>3</sub> (CoN<sub>6</sub>C<sub>4</sub>H<sub>20</sub>Cl<sub>3</sub>O<sub>12</sub>): C, H, N. Anal. [Co(NH<sub>3</sub>)<sub>5</sub>(5-norbornene-2-carbonitrile)](ClO<sub>4</sub>)<sub>3</sub>(CoN<sub>6</sub>C<sub>8</sub>H<sub>24</sub>Cl<sub>3</sub>O<sub>12</sub>): C, H, N. Anal. [Co(NH<sub>3</sub>)<sub>5</sub>NCCH=CH<sub>2</sub>](ClO<sub>4</sub>)<sub>3</sub>(CoN<sub>6</sub>C<sub>3</sub>H<sub>18</sub>Cl<sub>3</sub>O<sub>12</sub>): C, H, N, Co. Anal. [Co(NH<sub>3</sub>)<sub>5</sub>NC(CH<sub>2</sub>)<sub>4</sub>CN](ClO<sub>4</sub>)<sub>3</sub>(CoN<sub>7</sub>C<sub>6</sub>H<sub>23</sub>Cl<sub>3</sub>O<sub>12</sub>): C, H, N, Co. IR: 2260 (w), 2325 (w) cm<sup>-1</sup>. Anal. [Co(NH<sub>3</sub>)<sub>5</sub>NCCH<sub>3</sub>](ClO<sub>4</sub>)<sub>3</sub>(CoN<sub>6</sub>C<sub>2</sub>H<sub>18</sub>Cl<sub>3</sub>O<sub>12</sub>): C, H, N.

*Nitrile dimerization reactions of [Co(NH<sub>3</sub>)<sub>5</sub>NCCH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>](ClO<sub>4</sub>)<sub>3</sub> and [Co(NH<sub>3</sub>)<sub>5</sub>NCCH<sub>2</sub>CH=CH<sub>2</sub>](ClO<sub>4</sub>)<sub>3</sub>.* The complex was dissolved in a pH 6 phosphate or citrate buffer and allowed to react over 15 min. In the case of [Co(NH<sub>3</sub>)<sub>5</sub>NCCH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>]<sup>3+</sup> a white precipitate was deposited which was collected, washed with water and dried. Yield > 90 %, m.p. 140–160 °C. Anal. (C<sub>8</sub>H<sub>6</sub>N)<sub>n</sub>: C, H, N. MS [*m/e* (% rel.int)]: 232 (15, M), 116 (100) 89 (20). <sup>1</sup>H NMR [(CD<sub>3</sub>)<sub>2</sub>CO]: δ 1.95 (2 H, s, CH), 2.88 (2 H, s, CH), 3.60 (~0.1 H, s, CH), 3.80 (~0.1 H, s), 5.46 (10 H, s, 2ArH) 5.56 (10 H, s, 2ArH) relative to δ<sub>(CD<sub>3</sub>)<sub>2</sub>CO</sub>. After recrystallization from boiling acetic acid <sup>1</sup>H NMR ((CD<sub>3</sub>)<sub>2</sub>CO): δ 2.88 (2 H, s, 2CH) and 5.46 (10 H, s, 2ArH). For C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>CN <sup>1</sup>H NMR:

δ 1.88 (2 H, s, CH<sub>2</sub>), 5.30 (5 H, s, ArH) relative to δ<sub>(CD<sub>3</sub>)<sub>2</sub>CO</sub>. M.p. of recrystallized product 224–226 °C.

The reaction mixture from the [Co(NH<sub>3</sub>)<sub>5</sub>NCCH<sub>2</sub>CH=CH<sub>2</sub>]<sup>3+</sup> complex was extracted with dichloromethane and the solution dried over calcium sulfate. The solvent was removed on the vacuum evaporator leaving an oil. Anal. (C<sub>4</sub>H<sub>4</sub>N)<sub>n</sub>. <sup>1</sup>H NMR (CCl<sub>4</sub>): δ 2.6 (2 H, m), 3.6 (1H, m), 5.8 (4 H, m), 6.8 (1 H, m). For CH<sub>2</sub>=CHCH<sub>2</sub>CN <sup>1</sup>H NMR (CCl<sub>4</sub>): δ 3.05 (2 H, d, CH<sub>2</sub>), 5.4 (3 H, m, CH<sub>2</sub>=CH). MS [*m/e* (% rel.int)]: 132 (9, M), 131 (14), 105 (10), 92 (4), 79 (11), 66 (100), 52 (10), 39 (33). Samples of the complexes in pH 6 phosphate buffers were added to (1) a solution of 2,2-diphenyl-1-picrylhydrazyl in acetonitrile, (2) a solution of ~0.05 M Br<sub>2</sub> in a pH 6 phosphate buffer, (3) I<sub>2</sub> in a 1:1 CH<sub>3</sub>CN–pH 6 phosphate buffer.

*Reduction of [Co(NH<sub>3</sub>)<sub>5</sub>NCR](ClO<sub>4</sub>)<sub>3</sub> with NaBH<sub>4</sub>.* In a typical experiment [Co(NH<sub>3</sub>)<sub>5</sub>NCR](ClO<sub>4</sub>)<sub>3</sub> (2 × 10<sup>-3</sup> mol) was dissolved in a "Tris"/HCl buffer ["Tris" = tris(hydroxymethyl)aminomethane] at pH ~9 (30 ml) and mixed with a solution of NaBH<sub>4</sub> (Merck, 0.3 g) in the buffer (10 ml). After 6–8 min the reaction mixture was rapidly sorbed on an SP-Sephadex C-25 cation exchange column which had been washed with the buffer. When all the complex was sorbed the column was again washed carefully with the buffer to remove excess borohydride and the complex eluted with 0.5 M NaClO<sub>4</sub> at pH ~9. Some +2 amide complex was collected first followed by the main yellow product which analyzed for the corresponding aminopentammine complex. Yields ~50 %. For [Co(NH<sub>3</sub>)<sub>5</sub>NC(CH<sub>2</sub>)<sub>2</sub>CH(COCH<sub>3</sub>)<sub>2</sub>](ClO<sub>4</sub>)<sub>3</sub> also the carbonyl groups were reduced so that the isolated product analyzed for [Co(NH<sub>3</sub>)<sub>5</sub>NH<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>CH(CHOHCH<sub>3</sub>)<sub>2</sub>](ClO<sub>4</sub>)<sub>3</sub>. Anal. CoN<sub>6</sub>C<sub>8</sub>H<sub>34</sub>Cl<sub>3</sub>O<sub>14</sub>: C, N, H, Co. The other reduced nitrile complexes were: [Co(NH<sub>3</sub>)<sub>5</sub>NCCH<sub>3</sub>](ClO<sub>4</sub>)<sub>3</sub> with the product [Co(NH<sub>3</sub>)<sub>5</sub>NH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>](ClO<sub>4</sub>)<sub>3</sub>. Anal. CoN<sub>6</sub>C<sub>2</sub>H<sub>22</sub>Cl<sub>3</sub>O<sub>12</sub>: C, N, H. <sup>1</sup>H NMR (D<sub>2</sub>O): δ 1.16 (3 H, t, CH<sub>3</sub>), 2.36 (2 H, broad s, CH<sub>2</sub>) 3.40 (15 H, broad s, NH<sub>3</sub>). [Co(NH<sub>3</sub>)<sub>5</sub>NCCH<sub>2</sub>CO<sub>2</sub>C<sub>2</sub>H<sub>5</sub>](ClO<sub>4</sub>)<sub>3</sub> with the product [Co(NH<sub>3</sub>)<sub>5</sub>NH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CO<sub>2</sub>C<sub>2</sub>H<sub>5</sub>](ClO<sub>4</sub>)<sub>3</sub>. Anal. CoN<sub>6</sub>H<sub>26</sub>C<sub>5</sub>O<sub>11</sub>: C, N, H. <sup>1</sup>H NMR (D<sub>2</sub>O): δ 1.2 (3 H, t, CH<sub>3</sub>), 2.80 [4 H, broad s, (CH<sub>2</sub>)<sub>2</sub>], 3.60 (15 H, broad s, NH<sub>3</sub>), 4.20 (2 H, q, CH<sub>2</sub>). [Co(NH<sub>3</sub>)<sub>5</sub>NC(CH<sub>2</sub>)<sub>4</sub>CN](ClO<sub>4</sub>)<sub>3</sub> with the product [Co(NH<sub>3</sub>)<sub>5</sub>NH<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>CN](ClO<sub>4</sub>)<sub>3</sub>. Anal. C, H, N. IR: 2260 (w) cm<sup>-1</sup>.

*Reaction of [Co(NH<sub>3</sub>)<sub>5</sub>NCCH=CH<sub>2</sub>](ClO<sub>4</sub>)<sub>3</sub> with acetylacetone.* [Co(NH<sub>3</sub>)<sub>5</sub>NCCH=CH<sub>2</sub>](ClO<sub>4</sub>)<sub>3</sub> (5 g) was dissolved in water (300 ml) and rapidly mixed with a solution of acetylacetone (10 g) and sodium hydroxide (2 g) in water (100 ml). After 5 s excess concentrated perchloric acid was added to acidify the solution and quench the reaction. The

solution was reduced in volume on the vacuum evaporator. The yellow compound which crystallized out was collected and recrystallized from warm water (pH ~4) and addition of concentrated perchloric acid or solid sodium perchlorate. Yield 45% of a product which analyzed for  $[\text{Co}(\text{NH}_3)_5\text{NC}(\text{CH}_2)_2\text{CH}(\text{COCH}_3)_2](\text{ClO}_4)_3 \cdot \text{H}_2\text{O}$ . Anal.  $\text{CoN}_6\text{H}_{26}\text{C}_8\text{Cl}_3\text{O}_{14}$ : C, N, H, Co. IR: 2320 (w), 1740 (s)  $\text{cm}^{-1}$ . When the reaction mixture was left for 15 min before being acidified the product analyzed for  $[\text{Co}(\text{NH}_3)_5\text{NH}_2\text{CO}(\text{CH}_2)_2\text{CH}(\text{COCH}_3)_2](\text{ClO}_4)_3 \cdot \text{H}_2\text{O}$ . Yield 30%. Anal.  $\text{CoN}_6\text{C}_8\text{H}_{30}\text{Cl}_3\text{O}_{16}$ : C, N, H. IR: no absorption in the  $\text{C}\equiv\text{N}$  stretching region.

*Reaction of  $[\text{Co}(\text{NH}_3)_5\text{NCCH}=\text{CH}_2]\text{Cl}_3$  with nitromethane.*  $[\text{Co}(\text{NH}_3)_5\text{NCCH}=\text{CH}_2]\text{Cl}_3$  (2.2 g) was dissolved in water (25 ml) and added to a solution of nitromethane (7.2 g) in a "Tris"/HCl buffer at pH ~9 (100 ml). After 20 s the reaction was quenched by adding concentrated perchloric acid. The solution was diluted and sorbed on an SP-Sephadex C-25 cation exchange column and eluted with 0.3 M  $\text{NaClO}_4$ . The eluent containing the major component was taken down in volume on a vacuum evaporator and a yellow product crystallized out which analyzed for  $[\text{Co}(\text{NH}_3)_5\text{NC}(\text{CH}_2)_3\text{NO}_2](\text{ClO}_4)_3$ . Yield 45%. Anal.  $\text{CoN}_7\text{C}_7\text{H}_{21}\text{Cl}_3\text{O}_{14}$ : C, N, H, Co. IR: 2330 (w)  $\text{cm}^{-1}$ .  $^1\text{H NMR}$  ( $\text{D}_2\text{O}$ ):  $\delta$  2.50 (2 H, p,  $\text{CH}_2$ ), 3.20 (2 H, t,  $\text{CH}_2\text{CN}$ ), 3.90 (15 H, broad,  $\text{NH}_3$ ), 4.70 (2 H, t,  $\text{CH}_2\text{NO}_2$ ). When the reaction mixture was left for 15 min before being quenched the product analyzed for  $[\text{Co}(\text{NH}_3)_5\text{NH}_2\text{CO}(\text{CH}_2)_3\text{NO}_2](\text{ClO}_4)_3$ . Anal.  $\text{CoN}_7\text{H}_{23}\text{C}_4\text{Cl}_3\text{O}_{15}$ : C, N, H.

*Reaction of  $[\text{Co}(\text{NH}_3)_5\text{NCCH}=\text{CH}_2]\text{Cl}_3$  with malonitrile.* The complex (0.5 g) was dissolved in a "Tris"/HCl buffer at pH 9 saturated with malonitrile. After 10 s the reaction was quenched by the addition of concentrated perchloric acid and the reaction mixture sorbed on an SP-Sephadex C-25 cation exchange column. This was then eluted with 0.5 M  $\text{NaClO}_4$  and a yellow product was isolated which analyzed for  $[\{\text{Co}(\text{NH}_3)_5\text{NC}(\text{CH}_2)_2\}_2\text{C}(\text{CN})_2](\text{ClO}_4)_6 \cdot \text{H}_2\text{O}$ . Anal.  $\text{Co}_2\text{N}_{14}\text{C}_9\text{H}_{40}\text{Cl}_6\text{O}_{25}$ : C, N, H, Co.  $^1\text{H NMR}$  ( $\text{D}_2\text{O}$ ):  $\delta$  2.8 (2 H, t,  $\text{CH}_2\text{C}$ ), 3.6 (2 H, t,  $\text{CH}_2\text{CN}$ ).

*Reaction of  $[\text{Co}(\text{NH}_3)_5\text{NCCH}=\text{CH}_2]\text{Cl}_3$  with  $\text{PO}_4^{3-}$ .*  $[\text{Co}(\text{NH}_3)_5\text{NCCH}=\text{CH}_2]\text{Cl}_3$  (1 g) dissolved in water (10 ml) was rapidly mixed with a solution of  $\text{K}_3\text{PO}_4 \cdot \text{H}_2\text{O}$  (0.2 mol) and  $\text{K}_2\text{HPO}_4 \cdot 3\text{H}_2\text{O}$  (0.2 mol) in water (65 ml). After 30 s the reaction was quenched with concentrated perchloric acid (55 ml), filtered and diluted to 4 l. The reaction mixture was sorbed on an SP-Sephadex C-25 cation exchange column. The column was then washed with water and eluted with a pH 8 "Tris"/HCl buffer (0.05 M). A small orange band (1) separated out following the front of the eluent. This eluate was acidified with concentrated perchloric acid and reduced to a small

volume on a vacuum evaporator and a yellow compound crystallized out (6%). The column was then eluted with 0.3 M  $\text{NaClO}_4$  at pH 8. Three bands (2), (3) and (4) separated and all three compounds crystallized as the perchlorates upon acidification and evaporation to a small volume using a vacuum evaporator. Yield of band (2) 39%. Band (1) analyzed for  $[\text{Co}(\text{NH}_3)_5\text{NH}_2\text{CO}(\text{CH}_2)_2\text{OPO}_3\text{H}_2](\text{ClO}_4)_3 \cdot \text{H}_2\text{O}$ . Anal.  $\text{CoN}_6\text{C}_3\text{H}_{25}\text{P}\text{Cl}_3\text{O}_{18}$ : C, N, H, Co.  $^1\text{H NMR}$  ( $\text{D}_2\text{O}$ ):  $\delta$  2.8 (2 H, t,  $\text{CH}_2\text{CO}$ ), 4.1 (2 H, q,  $\text{CH}_2\text{OP}$ ), 3.4 (15 H, broad,  $\text{NH}_3$ ). Band (2) analyzed for  $[\text{Co}(\text{NH}_3)_5\text{NC}(\text{CH}_2)_2\text{OPO}_3](\text{ClO}_4)_4 \cdot 1\frac{1}{2}\text{HClO}_4$ . Anal.  $\text{CoN}_6\text{C}_3\text{H}_{20.5}\text{Cl}_{2.5}\text{PO}_{14}$ : C, N, H, Co, Cl, P.  $^1\text{H NMR}$  ( $\text{D}_2\text{O}$ ):  $\delta$  3.40 (2 H, t,  $\text{CH}_2\text{CN}$ ), 4.30 (2 H, q,  $\text{CH}_2\text{OP}$ ), 4.15 (3 H, broad, *cis*  $\text{NH}_3$ ), 3.75 (12 H, broad, *trans*  $\text{NH}_3$ ).  $^1\text{H NMR}$  ( $\text{D}_2\text{O}$ ) of bands (3) and (4) showed olefin signals and they were assumed to be unreacted acrylonitrile complex and acrylamide complex.

*Reaction of  $[\text{Co}(\text{NH}_3)_5\text{NCCH}_3](\text{ClO}_4)_3$  with  $\text{NaCN}$ .*  $[\text{Co}(\text{NH}_3)_5\text{NCCH}_3](\text{ClO}_4)_3$  (9 g) was dissolved in a mixture of  $\text{NaCN}$  (34 g),  $\text{Na}_2\text{EDTA}$  (7.5 g) and concentrated  $\text{HClO}_4$  (30.5 ml) in water (700 ml), pH ~10.5. After 20 min the solution was poured into 2.3 l  $\text{H}_2\text{O}$  containing 50 ml  $\text{HAc}$  and quickly sorbed on an SP-Sephadex C-25 cation exchange column. The column was eluted with 0.3 M  $\text{NaClO}_4$  until one orange band remained. This was taken off with 0.5 M  $\text{NaClO}_4$  and the complex crystallized by evaporation using a vacuum evaporator. Yield 40%. Anal.  $\text{CoN}_6\text{C}_{14}\text{H}_{21}\text{Cl}_3\text{O}_{12.5}$ : C, N, H, Co, Cl.  $^1\text{H NMR}$  [ $(\text{CD}_3)_2\text{SO}$ ]:  $\delta$  1.5 (3H, s,  $\text{CH}_3$ ), 3.0 (6 H, s, *cis*  $\text{NH}_3$ ), 3.2 (3 H, s, *trans*  $\text{NH}_3$ ), 5.6 (2 H, s,  $\text{CoNH}_2$ ), 6.4 (2 H, s,  $\text{NH}=\text{}$ ), 7.8 (2 H, broad s,  $\text{NH}_2-\text{C}=\text{}$ ), 8.2 (2 H, broad s,  $\text{NH}_2-\text{C}=\text{}$ ).

$\alpha$ -Alanine was produced by decomposing the product with  $\text{H}_2\text{S}$ . The complex was dissolved in  $\text{H}_2\text{O}$  and treated with a stream of  $\text{H}_2\text{S}$ . After filtration the solution was reduced to dryness and then dissolved in slightly acidic water (pH ~3) and sorbed on a cation exchange column (Dowex 50 W-X2, 200-400 mesh,  $\text{NH}_4^+$  form). The column was washed with water (pH ~3) and then eluted with 1 M  $\text{NH}_3$ . The eluate was reduced to dryness to give a white product.  $^1\text{H NMR}$  ( $\text{D}_2\text{O}$ ):  $\delta$  1.5 (s).

The product was refluxed with 1 M  $\text{HCl}$  for 1  $\frac{1}{2}$  h and the resulting material isolated.  $^1\text{H NMR}$  ( $\text{D}_2\text{O}$ ):  $\delta$  1.6 (3 H, d,  $\text{CH}_3$ ), 4.1 (1 H, q, CH). An authentic sample of  $\alpha$ -alanine.HCl gave an identical  $^1\text{H NMR}$  spectrum.  $\alpha$ -Alanine was isolated by adjusting an aqueous solution to pH 6 with aniline and adding ethanol. M.p. = 280-290 °C. M.p. for  $\alpha$ -alanine is 295 °C. Anal. Found: C 39.02; H 8.49; N 14.83. Calc. for  $\text{C}_3\text{H}_7\text{NO}_2$ : C 40.44; H 7.91; N 15.72.

## RESULTS AND DISCUSSION

**Syntheses.** A simple and direct method to prepare cobalt(III) pentaammine nitrile complexes is to treat  $[\text{Co}(\text{NH}_3)_5\text{N}_3](\text{ClO}_4)_3$  with an excess of  $\text{NOCF}_3\text{SO}_3$  in a solution or suspension of the complex in the nitrile containing some trimethyl phosphate to assist dissolution. The initially formed complex may be wholly or partly  $[\text{Co}(\text{NH}_3)_5\text{TMP}]^{3+}$  (TMP = trimethyl phosphate) which on standing exchanges TMP for the nitrile. In the instances when this method was used the  $\text{NO}^+$  did not attack double bonds nor aromatic rings. The nitrile complex was then isolated from the reaction mixture by the addition of ether and recrystallization of the precipitated product from water. Care had to be taken with solutions of the  $\text{C}_6\text{H}_5\text{CH}_2\text{CN}$  and  $\text{CH}_2=\text{CHCH}_2\text{CN}$  complexes to keep them acidic at all times to minimize decomposition.

The coordinated nitrile groups were easily characterized by their IR spectra. They all showed  $\text{C}\equiv\text{N}$  stretching absorptions at  $\sim 2330\text{ cm}^{-1}$  while the absorptions of the uncoordinated nitriles appeared at  $\sim 2260\text{ cm}^{-1}$ . The adiponitrile complex spectrum displayed both as expected for a compound with one coordinated and one uncoordinated nitrile group. The same result was previously observed for  $[\text{Co}(\text{NH}_3)_5\text{NCCH}_2\text{CN}]^{3+}$ .<sup>10</sup>

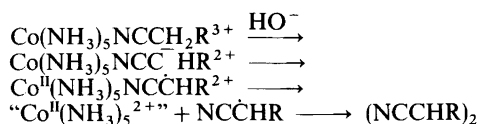
**Nitrile radical formation.** When the complexes  $[\text{Co}(\text{NH}_3)_5\text{NCCH}_2\text{C}_6\text{H}_5](\text{ClO}_4)_3$  or  $[\text{Co}(\text{NH}_3)_5\text{NCCH}_2\text{CH}=\text{CH}_2](\text{ClO}_4)_3$  were dissolved in neutral or basic aqueous solution, immediate decomposition of the complexes was observed with the production of cobalt(II),  $\text{NH}_3$  and organic products. For  $[\text{Co}(\text{NH}_3)_5\text{NCCH}_2\text{C}_6\text{H}_5]^{3+}$  a white precipitate was deposited which analysed for  $(\text{C}_8\text{H}_6\text{N})_n$ . Its mass spectrum indicated it to be a molecule with a molecular weight of 232 ( $\text{C}_{16}\text{H}_{12}\text{N}_2$ ) which readily splits into two halves. The  $^1\text{H}$  NMR spectrum exhibited four principal resonances and two minor ones. After recrystallization from boiling acetic acid only two of the resonances remained. They integrated as 1:5. Both spectra were different from that of the starting material  $\text{C}_6\text{H}_5\text{CH}_2\text{CN}$ . When solutions of the free radical 2,2-diphenyl-1-hydrazyl, bromine, or iodine were added to the decomposing mixture their colours faded. During the same period of time no disappearance of colour was observed under identical conditions when the complexes were not present.

The data are consistent with an almost quantitative formation of the dimer 2,3-diphenylsuccino-

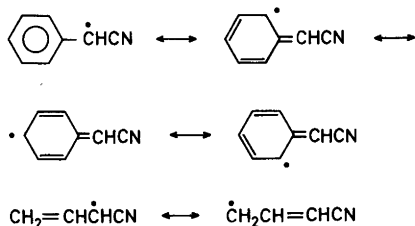
nitrile,  $\text{C}_6\text{H}_5\text{CH}(\text{CN})\text{CH}(\text{CN})\text{C}_6\text{H}_5$ , (M.W. 232.26) in an approximately equal mixture of the *meso* and racemic forms with minor amounts of two other isomers. On recrystallization from hot acetic acid the racemic form of  $\text{C}_6\text{H}_5\text{CH}(\text{CN})\text{CH}(\text{CN})\text{C}_6\text{H}_5$  is transformed into the *meso* form.<sup>15</sup> This means that the two resonances in the  $^1\text{H}$  NMR spectrum of the recrystallized product are due to 2 CH protons ( $\delta$  2.88) and 10 aromatic protons ( $\delta$  5.46) arising from *meso*  $\text{C}_6\text{H}_5\text{CH}(\text{CN})\text{CH}(\text{CN})\text{C}_6\text{H}_5$  and that the resonances at  $\delta$  1.95 and 5.56 in the original spectrum arise from the racemic isomer. The melting point of 224–226 °C was lower than that recorded for the pure *meso* form, 238–240 °C,<sup>15</sup> presumably because of traces of the racemic form (M.p. 160 °C).<sup>16</sup> 2,3-Diphenylsuccinonitrile has been synthesized by several methods<sup>15</sup> including condensation and photochemical methods giving good yields (70–90 %) but requiring relatively long reaction times and producing predominantly the *meso* form. The method presented here yields the product in seconds by dissolving coordinated benzyl nitrile in water and produces 50 % of the racemic form which can be obtained pure by fractional crystallization.<sup>16</sup>

The  $[\text{Co}(\text{NH}_3)_5\text{NCCH}_2\text{CH}=\text{CH}_2]^{3+}$  complex reacted under similar conditions giving cobalt(II),  $\text{NH}_3$  and an oil which analysed for  $(\text{C}_4\text{H}_4\text{N})_n$ . The  $^1\text{H}$  NMR spectrum revealed four multiplets which integrated roughly as 2:1:4:1. No resonances corresponding to the  $\text{CH}_2$  protons in the original nitrile  $\text{CH}_2=\text{CHCH}_2\text{CN}$  were observed. The mass spectrum indicated a molecular weight of 132 ( $\text{C}_8\text{H}_8\text{N}_2$ ) and again showed compounds which readily split into two halves. Gas chromatography of the product indicated it to be a rather complex mixture. The results are consistent with an isomeric mixture of dimeric nitriles with the formula  $(\text{CH}_2=\text{CHCH}(\text{CN}))_2$ .

The rapid formation of dimeric nitriles in these decomposition reactions can be explained by the fast deprotonation of the methylene group of the coordinated nitrile, followed by a rapid oxidation of the coordinated carbanion by cobalt(III) to the radical which then dissociates from the labile cobalt(II)  $(\text{NH}_3)_5^{2+}$  ion and dimerizes (Scheme 1)



Scheme 1.



Scheme 2.

or reacts with other radicals or radical trapping agents. However, reactions between radical and coordinated radical cannot be excluded. The presence of radicals is supported by the observation of the reactions with 2,2-diphenyl-1-hydrazyl and bromine or iodine which are known radical trapping agents.

In both the instances above we are dealing with nitrile radicals which are resonance-stabilized (Scheme 2). This could give rise to several isomers when the radicals react with each other. However, for the benzyl nitrile complex, by far the major product is  $C_6H_5CH(CN)CH(CN)C_6H_5$  (DL + meso) with only small amounts of two other isomers. The resonance forms of the allyl nitrile radical suggest the possible dimerization isomers:  $[CH_2=CHCH(CN)]_2$  (DL + meso),  $(NCCH=CHCH_2)_2$  and  $CH_2=CHCH(CN)CH_2CH=CHCN$ . Interpretation of the  $^1H$  NMR resonances as being due to A:  $\delta$  2.6,  $-CH_2-$ ; B:  $\delta$  3.6,  $CHCN$ ; C:  $\delta$  5.8,  $CH_2=$  and  $-CH=$ ; and D:  $\delta$  6.8,  $=CHCN$  along with the integration A:B:C:D = 2:1:4:1 indicates either the formation of the unsymmetrical isomer or a 1:1 mixture of the two symmetrical isomers, and possibly some of the unsymmetrical one. The last suggestion seems the most likely as in a fast dimerization of two very reactive radicals the exclusive formation of the unsymmetrical dimer would not be expected.

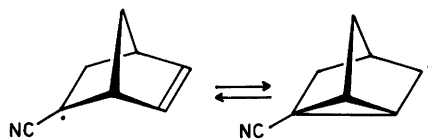
The  $[Co(NH_3)_5NCCH_2NHCOCCH_3]^{3+}$  complex partly decomposed in neutral or basic solution. If resonance is a requirement for the formation of the nitrile radicals it may in this case arise from the presence of the enol form:  $NCCH_2NHCOCCH_3 \leftrightarrow NCCH_2NC(OH)CH_3$  giving the radicals  $NC\dot{C}HN=(OH)CH_3 \leftrightarrow NCCH=N\dot{C}(OH)CH_3$ . However, competition for hydrolysis to the coordinated amide was here the stronger factor. When the benzylcyanide and allylcyanide complexes were treated with strongly basic solution some hydrolysis was also observed. By allowing the decomposi-

tion to take place at a low pH this side reaction was depressed. Other nitrile complexes such as  $[Co(NH_3)_5NCCH_2CO_2C_2H_5]^{3+}$ ,  $[Co(NH_3)_5NCCH_2CO_2H]^{3+}$  and  $[Co(NH_3)_5NCCH_2CN]^{3+}$  have earlier been shown to initiate acrylonitrile polymerisation by radical formation.<sup>10</sup> The radicals formed from these complexes are also resonance stabilized.

The  $[Co(NH_3)_5NCCH_2NHCOCCH_3](ClO_4)_3$  complex was prepared in the hope that it might prove useful in the synthesis of  $\alpha$ -substituted amino acids. By treating the complex in DMSO with alkyl halides in the presence of an equivalent amount of base it was hoped to be able to alkylate the methylene group as was the case for  $[Co(NH_3)_5NCCH_2CO_2Et]^{3+}$ .<sup>10</sup> Base hydrolysis of the coordinated nitrile and removal of the ligand from the complex would then lead to  $NH_2COCR^1R^2NHCOCCH_3$  ( $R^1=R^2$  or H) which on hydrolysis would give  $HO_2CCR^1R^2NH_2$ . However, because of the radical formation following the addition of base the complex decomposed before reacting with the alkyl halide.

The prospects for stabilizing radicals and bond migration in a homo-conjugated system were examined by preparing the complex  $[Co(NH_3)_5(2\text{-endo-cyano-5-norbornene})](ClO_4)_3$ . Homoallylic participation potentially allows products derived from the involvement of the two radicals shown in Scheme 3, however no decomposition was observed when this complex was dissolved in neutral or basic solution thereby discarding homo-conjugation as a likely stabilizing factor for the formation of nitrile radicals at least in this system.

The radical-producing nitrile complexes were all stable in dilute aqueous acid solutions, but decomposed rapidly in unbuffered neutral solutions and in basic media. By choosing an appropriate pH of the aqueous solution it is possible to control the rate of deprotonation and thereby the production of the radicals. Decomposition of  $[Co(NH_3)_5NCCH_2C_6H_5]^{3+}$  and  $[Co(NH_3)_5NCCH_2CH=CH_2]^{3+}$  was still observed at pH 4 but was much slower at pH 3. The complexes as the perchlorate



Scheme 3.

salts, are slightly soluble in some organic solvents such as  $\text{HCONMe}_2$ ,  $\text{Me}_2\text{SO}$ ,  $\text{Me}_2\text{CO}$  and  $\text{MeCN}$  but decompose rapidly unless acid is added. The same dinitrile dimers were obtained with  $[\text{Co}(\text{NH}_3)_5\text{NCCH}_2\text{C}_6\text{H}_5]^{3+}$  in acetonitrile as in aqueous solution.

These reactions show a particularly facile way of producing a carbanion and then a radical adjacent to a strong electron-withdrawing group under mild conditions. The process is easily controlled by the pH of the aqueous solution and the subsequent one-electron transfer is fast. In some instances useful organic synthesis via carbanion and radical generation could be conducted by this mixture of intra- and intermolecular processes.

*Reduction of coordinated nitriles by  $\text{NaBH}_4$ .* Normally nitriles require potent reducing agents such as  $\text{LiAlH}_4$  in a non-aqueous medium to generate the amine. However, if a strong electron-withdrawing group such as a metal ion is applied to the nitrile moiety the carbon centre becomes more susceptible to attack by  $\text{H}^-$  or  $\text{BH}_4^-$  and the prospect for a more facile reduction arises. The problem of a reduction of the metal ion also exists and the selectivity between the two processes is a key component in such a strategy.

$[\text{Co}(\text{NH}_3)_5\text{NCCH}_3]^{3+}$  was treated with excess  $\text{NaBH}_4$  in a pH  $\sim 9$  buffer for 7–8 min. After separation of the complexes on a cation exchange column the main product was found to be  $[\text{Co}(\text{NH}_3)_5\text{NH}_2\text{CH}_2\text{CH}_3]^{3+}$  together with some  $[\text{Co}(\text{NH}_3)_5\text{NHCOCH}_3]^{2+}$  and cobalt(II). When other coordinated nitriles such as  $[\text{Co}(\text{NH}_3)_5\text{NCCH}_2\text{CO}_2\text{C}_2\text{H}_5]^{3+}$ ,  $[\text{Co}(\text{NH}_3)_5\text{NC}(\text{CH}_2)_4\text{CN}]^{3+}$  and  $[\text{Co}(\text{NH}_3)_5\text{NC}(\text{CH}_2)_2\text{CH}(\text{COCH}_3)_2]^{3+}$  were treated similarly the corresponding amine complexes were also recovered from the reaction mixtures. Attempts to follow the rates of reduction were frustrated by the side reactions, mainly of the reducing ion  $\text{BH}_4^-$ . The formation of traces of cobalt(II) species prevented the reaction from being followed by  $^1\text{H}$  NMR and the evolution of  $\text{H}_2$  from the reaction between  $\text{BH}_4^-$  and water made it difficult to follow the rates by spectrophotometric methods. However, an estimated half life of  $\sim 1$  min for the reduction of  $[\text{Co}(\text{NH}_3)_5\text{NCCH}_3]^{3+}$  was obtained by sampling the reaction mixture over intervals and separating the components by ion exchange chromatography. The rate of reaction showed some dependence on the  $\text{BH}_4^-$  concentration but the quantification was difficult to assess accurately. The yield of amine complex seemed

markedly dependent on the purity of  $\text{NaBH}_4$ . When uncoordinated acetonitrile was treated with  $\text{NaBH}_4$  under identical circumstances no sign of reduction was apparent over 10 days. By this time a substantial amount of the  $\text{BH}_4^-$  ion had decomposed but the  $^1\text{H}$  NMR spectra still indicated the presence of H–B signals and thus reducing capacity. It appears therefore that reduction of the coordinated nitrile is enhanced by  $> 10^4$  over the rate of the uncoordinated one. For the adipic nitrile and the cyanoacetic ethylester complexes only the nitrile groups attached to cobalt(III) were reduced while the other functional groups were unaffected so that some specificity was built into the reaction. Further, no reduction was observed when the N-bound acetamide complex  $[\text{Co}(\text{NH}_3)_5\text{NHCOCH}_3]^{2+}$  was treated with  $\text{NaBH}_4$  for 20 min at room temperature.

The process demonstrates a rapid reduction of a nitrile under very mild conditions in an aqueous medium. In the present cases the complexes are kinetically inert but the implication is that the reduction of a nitrile which is predominantly  $\alpha$ -bound to a metal ion should be accelerated for labile complexes as well, provided the complexes are stable around pH 9–10. Metal oxidation states such as Co(II), Cu(II), Ni(II), Pt(II) and Os(II) have been used to accelerate reduction of nitrile by  $\text{BH}_4^-$  in hydroxylic as well as non-hydroxylic solvents.<sup>17</sup> However, in contrast to the chemistry above these reagents were also capable of reducing amides and nitro compounds to primary amines and the reduction could arise via a metal hydride complex rather than directly from the  $\text{BH}_4^-$  reagent. The effective metals are those which readily form metal hydrides. In the present case the Co–N–C entity remains intact during the reduction, indicating that the reducing agent is  $\text{BH}_4^-$  and not a cobalt hydride.

The yields of reduced nitrile complexes were usually  $\sim 50\%$ . The question arises whether the remaining organic residues appeared as free amines or unreacted free nitriles in the reaction mixture. This problem needs further exploration.

The same reactions conducted in more acidic media lead to a preferential reduction of the metal centre presumably *via* the  $\text{B}_2\text{H}_6$  reagent. The low specificity of  $\text{BH}_4^-$  ion for the metal centre compared with coordinated unsaturated organic functions is an especially interesting specificity giving rise to real synthetic potential. We presume that whereas  $\text{B}_2\text{H}_6$  adds rapidly to the filled *d* electron orbitals of the metal ion, the  $\text{BH}_4^-$  anion has more

difficulty doing so and prefers a nucleophilic role at the unsaturated organic moiety rather than the electron-rich metal centre.

**Cyanoethylation reactions.** A variety of compounds possessing labile hydrogen atoms add to acrylonitrile in the presence of an alkaline catalyst with the formation of molecules containing the  $-\text{CH}_2\text{CH}_2\text{CN}$  moiety in a so-called cyano-ethylation reaction:  $\text{RH} + \text{CH}_2 = \text{CHCN} \rightarrow \text{RCH}_2\text{CH}_2\text{CN}$ . The cyanide group introduces a polarization in the acrylonitrile molecule  $\overset{+\delta}{\text{C}}\text{H}_2 = \text{CHC} \equiv \overset{-\delta}{\text{N}}$  facilitating the attack of the deprotonated reagent  $\text{R}^-$  at  $\overset{+\delta}{\text{C}}\text{H}_2$ . In aqueous solution these reactions are slow and usually occur with multiple additions in the presence of labile methyl or methylene groups, e.g.  $\text{RCH}_3 + \text{CH}_2 = \text{CHCN} \rightarrow \text{RCH}_2\text{CH}_2\text{CH}_2\text{CN} \rightarrow \text{RCH}(\text{CH}_2\text{CH}_2\text{CN}) \rightarrow \text{RC}(\text{CH}_2\text{CH}_2\text{CN})_3$ . It was of interest therefore to investigate whether the activating influence of a metal ion would extend to the distant carbon atom for these carbanion addition reactions and whether there is any selectivity in these additions.

When a large excess of half-neutralized acetylacetone (pH  $\sim 9$ ) was added to an aqueous solution of  $[\text{Co}(\text{NH}_3)_5\text{NCCH}=\text{CH}_2]^{3+}$  addition of  $\text{CH}(\text{COCH}_3)_2$  occurred within 5 s producing  $[\text{Co}(\text{NH}_3)_5\text{NC}(\text{CH}_2)_2\text{CH}(\text{COCH}_3)_2]^{3+}$  ( $\sim 45\%$ ). The product was characterized by its  $^1\text{H}$  NMR spectrum, IR spectrum and by elemental analysis. Some reduction to cobalt(II) occurred during the reaction and when left in the basic reaction mixture hydrolysis of the nitrile complex to the coordinated amide complex  $[\text{Co}(\text{NH}_3)_5\text{NHCO}(\text{CH}_2)_2\text{CH}(\text{COCH}_3)_2]^{2+}$  took place. For uncoordinated acrylonitrile under the same conditions the additions are very slow ( $t_3 > 7$  h for acetylacetone) which indicates an acceleration factor  $> 10^4$  for the coordinated nitrile.

Nitro-methane also added to the acrylonitrile complex in a fast reaction producing  $[\text{Co}(\text{NH}_3)_5\text{NC}(\text{CH}_2)_3\text{NO}_2]^{3+}$  in  $\sim 50\%$  yield. Again the nitrile complex hydrolyzed to the corresponding amido complex when left in the basic reaction mixture.  $^1\text{H}$  NMR, IR spectra and elemental analysis confirmed the formulae.

Most interestingly  $\text{PO}_4^{3-}$  added to the double bond in coordinated acrylonitrile when  $[\text{Co}(\text{NH}_3)_5\text{NCCH}=\text{CH}_2]\text{Cl}_3$  was treated with a concentrated solution of  $\text{K}_3\text{PO}_4$  and  $\text{K}_2\text{HPO}_4$  (pH = 11.3), producing the coordinated monophosphate ester which crystallized as  $[\text{Co}(\text{NH}_3)_5\text{NC}(\text{CH}_2)_2\text{OPO}_3] \cdot$

$\text{ClO}_4 \cdot 1\frac{1}{2}\text{HClO}_4$  (39%). Some  $[\text{Co}(\text{NH}_3)_5\text{NH}_2\text{CO}(\text{CH}_2)_2\text{OPO}_2\text{H}_2](\text{ClO}_4)_3$  product arising from base hydrolysis of the nitrile complex was formed as well (6%). Kinetic studies of the reaction of  $[\text{Co}(\text{NH}_3)_5\text{NCCH}=\text{CH}_2]^{3+}$  in a solution containing 0.5 M  $\text{K}_3\text{PO}_4$  and 0.5 M  $\text{K}_2\text{HPO}_4$  (pH = 11.27, 25 °C) revealed two pseudo first-order rate constants  $k_{\text{obs}}^1 = 49.5 \times 10^{-3} \text{ s}^{-1}$  and  $k_{\text{obs}}^2 = (9.7 \pm 0.4) \times 10^{-3} \text{ s}^{-1}$ . When the isolated  $[\text{Co}(\text{NH}_3)_5\text{NC}(\text{CH}_2)_2\text{OPO}_3]\text{ClO}_4$  complex was treated similarly only one rate was observed with  $k_{\text{obs}}^1 = (9.6 \pm 0.2) \times 10^{-3} \text{ s}^{-1}$ . The rate constant  $k_{\text{obs}}^1$  corresponds to that for the base hydrolysis of  $[\text{Co}(\text{NH}_3)_5\text{NCCH}=\text{CH}_2]^{3+}$  ( $k_1^1 = 27 \text{ M}^{-1} \text{ s}^{-1}$ );  $k_2$  for this reaction at 25 °C,  $\mu = 1.0$ , was  $35 \text{ M}^{-1} \text{ s}^{-1}$ .<sup>10</sup> The fact that  $k_{\text{obs}}^2 = k_{\text{obs}}^1$  implies that the second rate observed in the reaction of  $[\text{Co}(\text{NH}_3)_5\text{NCCH}=\text{CH}_2]^{3+}$  with phosphate is due to base hydrolysis of  $[\text{Co}(\text{NH}_3)_5\text{NC}(\text{CH}_2)_2\text{OPO}_3]^+$  to the corresponding amide complex with a second-order rate constant of  $k_2^2 = k_2^1 = 5.2 \pm 0.2 \text{ M}^{-1} \text{ s}^{-1}$ . The product  $[\text{Co}(\text{NH}_3)_5\text{NH}_2\text{CO}(\text{CH}_2)_2\text{OPO}_3\text{H}_2](\text{ClO}_4)_3$  was then isolated from the reaction mixture and characterized by  $^1\text{H}$  NMR spectroscopy and elemental analysis.

These results demonstrate that  $\text{PO}_4^{3-}$  adds to the coordinated acrylonitrile double bond at a rate comparable to the base hydrolysis rate of the coordinated nitrile. That  $\text{PO}_4^{3-}$  was the reactive nucleophile was demonstrated by the fact that no addition took place during the same period with  $\text{HPO}_4^{2-}$ . Addition of  $\text{P}_2\text{O}_7^{4-}$  and  $\text{O}_2\text{P}(\text{OCH}_3)_2^-$  also proved unsuccessful. The reaction described here is interesting in that it demonstrates the very fast addition of  $\text{PO}_4^{3-}$  to a double bond in aqueous solution producing the monophosphate ester as the only product while most phosphate ester syntheses give rise to a mixture of mono- and diphosphate esters. Attempts to follow the reaction between free acrylonitrile and phosphate were frustrated for lack of a solvent common to both reagents.

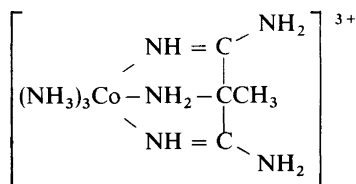
The isolated addition products were mostly the monocyanoethylated compounds. Smaller amounts of yellow compounds were detected at the top of the cation exchange columns after elution of the main products. These were hard to elute and may have consisted of higher substituted complexes which would be highly charged, for example  $\{(\text{Co}(\text{NH}_3)_5\text{NC}(\text{CH}_2)_2)_2\text{C}(\text{COCH}_3)_2\}^{6+}$  and  $\{\text{Co}(\text{NH}_3)_5\text{NC}(\text{CH}_2)_2\}_2\text{CHNO}_2^+$ . However, the amounts were very small and no attempts were made to isolate them. Only in the case of

malononitrile did the isolated compound analyze as the dinuclear complex.

Besides offering extremely fast reactions the coordinated acrylonitrile thus has the additional benefit of producing primarily monocynoethylated products which are easily separated from smaller amounts of other addition products.

The ligands in all these cobalt(III) complexes can be readily removed from the metal by reduction with acidic  $\text{BH}_4^-$ ,  $\text{V}^{2+}$ ,  $\text{Cr}^{2+}$  or by treatment with  $\text{CN}^-$  or  $\text{S}^-$ .

The reaction of cyanide with  $[\text{Co}(\text{NH}_3)_5\text{NCCH}_3]\text{Cl}_3$ . The product from the reaction of  $[\text{Co}(\text{NH}_3)_5\text{NCCH}_3]^{3+}$  and cyanide at pH  $\sim 10$  was found from an X-ray crystallographic analysis<sup>13</sup> to be the tridentate bis(amidine)aminomethylmalonate complex.

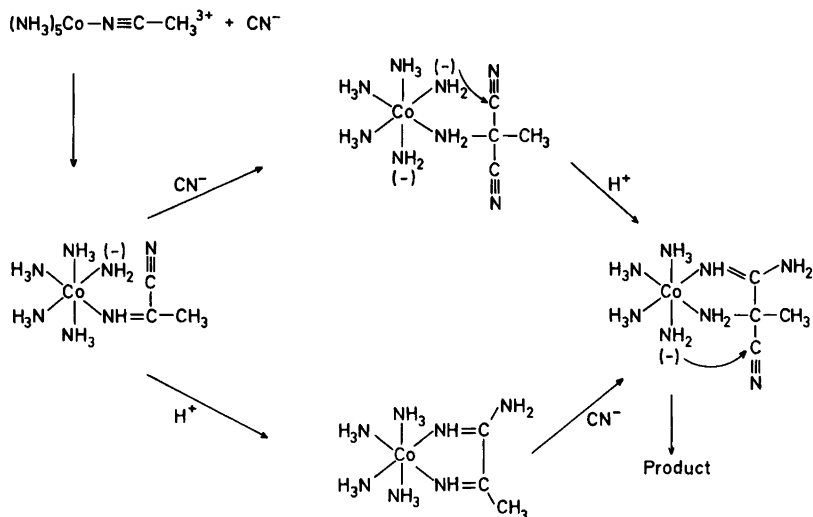


The compound was further characterized by its elemental analysis and  $^1\text{H}$  NMR spectrum.

The reaction is assumed to proceed initially by the attack of  $\text{CN}^-$  at the nitrile carbon producing a coordinated imine, Scheme 4. There appears to be

two possibilities for the next step. It may involve deprotonation of a neighbouring NH group followed by nucleophilic attack of coordinated amide at the nitrile C atom to produce a chelated amidine. The rate constants for proton exchange with coordinated  $\text{NH}_3$  are large ( $\sim 10^6 \text{ M}^{-1}\text{s}^{-1}$ ,  $25^\circ\text{C}$ ) in basic media even though the  $\text{pK}_a$  of the coordinated ammonia is  $\sim 14-16$ . These properties allow for rapid proton transfer in the routes for the suggested condensation which has been observed in other cases.<sup>18</sup> This reaction is then followed by the addition of another  $\text{CN}^-$  and a second intramolecular amide addition results in the tridentate bis-(amidine)aminomethylmalonate complex. The other possibility is the attack of another  $\text{CN}^-$  on the coordinated imine followed by intramolecular addition of *cis* amide ions. It is known from other cases that coordinated imines are more susceptible to attack by  $\text{CN}^-$  than the original nitrile<sup>19</sup> which explains why only the tridentate complex was observed.

Release of the diamidine ligand from the complex in aqueous solution followed by rapid hydrolysis should result in the production of amino methylmalonamide which readily hydrolyzes and decarboxylates to  $\alpha$ -alanine. This was also observed. On treating an aqueous solution of the complex with  $\text{H}_2\text{S}$  a white compound was isolated whose  $^1\text{H}$  NMR spectrum was consistent with  $\text{CH}_3\text{C}(\text{NH}_2)(\text{CO}_2\text{NH}_4)_2$ . When this compound was refluxed in acid solution the isolated product exhibited a  $^1\text{H}$



Scheme 4.



NMR spectrum identical to that of  $\alpha$ -alanine.HCl and finally  $\alpha$ -alanine itself was isolated and analyzed.

The reaction between  $\text{CN}^-$  and a coordinated nitrile thus introduces the possibility of a general amino acid synthesis from nitriles and a means of labelling the carboxyl group.

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