Experimental Section

The physical properties of all compounds used in this study were previously reported.[3] Most rate measurements were made with a Unicam SP-800 recording uv spectrophotometer at 6-, 20-, and 60-min single-wavelength time scans (or by using a scale expander and slave recorder), with the sample in a 1-cm fused silica cell with a Teflon stopper in a controlled-temperature ($\pm 0.1°$) cell block. For very slow rates the reaction was carried out in a 50-ml flask immersed in a constant-temperature bath. Aliquots (3 ml) were removed periodically, quenched by cooling, and measured for ultraviolet absorbance.

In dilute solution rates could be conveniently followed by absorbance (A) measurements at about 280 nm for most compounds, but in concentrated acid the wavelength for maximal absorbance change was highly dependent upon the type of acyl substituent; in general, measurements were taken at wavelengths near 230 nm and/or near 300 nm. It was found that k_ψ was invariant with substrate concentration over the range of 5×10^{-5}–2×10^{-3} M, and k_ψ obtained from rates of product formation was shown to equal k_ψ obtained from rates of substrate disappearance. Products were shown to be stable under the reaction conditions, since after seventeen half-lives in every case the isosbestic points of spectral curves were still sharply defined. Rates were followed for at least two half-lives, and infinity values were taken after six–ten half-lives. The final spectrum in all cases was identical with the spectrum of thiourea and the carboxylic acid in the appropriate concentration of sulfuric acid. For slower reactions Guggenheim's method[29] was used to obtain the rate. All calculations were done by an IBM-360 computer and a least-squares program for log ($A_t - A_\infty$) *vs.* time was used throughout. In nearly every case correlation coefficients of better than 0.998 for eight points were obtained.

For very fast reactions, for which a sampling technique was not possible, 3 ml of acid was placed in a stoppered cell, which was left to reach thermal equilibrium in the cell block for a minimum of 10 min. Methanolic stock solution (8–10 μl) of the *N*-acylthiourea was then injected into the solution, which was shaken and placed back into the thermostated cell block; spectra were recorded after a 3- to 10-min reequilibration. For kinetic runs carried out in a thermostated 50-ml flask, 50 ml of acid was placed in the flask and left for a minimum of 15 min to reach thermal equilibrium. A 10-μl sample of stock solution of *N*-acylthiourea was then injected by use of a Hamilton syringe with a Chaney adaptor, the solution was well shaken, and after 0.5 hr back in the bath, the initial aliquot was taken.

Acknowledgment. Financial support of the National Research Council of Canada is gratefully acknowledged.

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[29] K. J. Laidler, "Chemical Kinetics," 2nd ed, McGraw-Hill, New York, N. Y., 1965, p 14.

Hydrolysis of Coordinated Nitriles to Carboxamide Complexes of Pentaamminecobalt(III)

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Abstract: It has been found that benzonitrile and 3- and 4-cyanophenol coordinated to pentaamminecobalt(III) are hydrolyzed in alkaline solution to the corresponding nitrogen-bonded carboxamido product. The kinetics of the reaction has been studied and found to be first order in hydroxide ion concentration, with rate constant (M^{-1} sec^{-1}, 25.6°), $\Delta H^{\ddagger}$ (kcal mol^{-1}), and $\Delta S^{\ddagger}$ (cal mol^{-1} deg^{-1}), for benzonitrile, 18.8, 16.6, 2.7, for 3-cyanophenol, 3.57, 15.1, −5.5, and for 4-cyanophenol, 0.18, 16.3, −7.4, respectively. The product of the hydrolysis is converted in acid solution to $(NH_3)_5CoNH_2COC_6H_5$ and the pK_a of the latter has been determined to be 1.65 at 25° in 1 M $LiClO_4$.

It has been observed previously[1,2] that metal ions can catalyze the hydrolysis of nitriles to the corresponding carboxamide. During work to extend previous studies[3] on nitrogen-bonded carboxamide complexes of pentaamminecobalt(III) it was observed that coordinated nitriles in this system are easily hydrolyzed to the desired N-bonded carboxamide product. The kinetics of this process and the characterization of the benzamide product are described here.

The kinetics have been studied in order to provide further insight into the mechanism for the catalyzed hydrolyses in the more labile copper(II)[2] and nickel(II) systems. In the latter systems there is the possibility that a coordinated hydroxide ion is actually attacking the nitrile, although arguments against this possibility have been made by Breslow, *et al.*[1] With pentaamminecobalt(III) no coordinated groups can be reacting and attack by free hydroxide ion must be involved. The reaction with nickel(II) seems unusual in that the rate enhancement is primarily associated with a $\Delta S^{\ddagger}$ effect, and it is of interest to determine if this is also true for $(NH_3)_5Co^{3+}$.

Experimental Section

All the nitrile complexes can be prepared by the same general procedure. A mixture of aquopentaamminecobalt(III) perchlorate (5 g), a fivefold molar excess of the nitrile, and 2–3 g of molecular sieve, and 50 ml of trimethyl phosphate was heated on a steam bath at 70–80° until the solution turned yellow-brown (1–2 hr). The molecular sieve was removed by filtration and the filtrate treated with *sec*-butyl alcohol (~800 ml) to precipitate the crude product. This product may be purified by recrystallization of the perchlorate salt from aqueous solution or by ion exchange chromatography on Rexyn-102H weak acid cation exchange resin. In the latter method the eluting agent was aqueous sodium chloride and the procedure described previously[3] was used to isolate the product. The properties reported here all refer to ion-exchanged materials.

The N-bonded benzamide complex was prepared from the benzonitrile complex by dissolving the latter in a minimum amount of

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[1] R. Breslow, R. Fairweather, and J. Keana, *J. Amer. Chem. Soc.*, **89**, 2135 (1967).

[2] (a) S. Komiya, S. Suzuki, and K. Watanabe, *Bull. Chem. Soc. Jap.*, **44**, 1440 (1971); (b) S. Suzuki, M. Nakahura, and K. Watanabe, *ibid.*, **44**, 1441 (1971); (c) K. Sakai, T. Ito, and K. Watanabe, *ibid.*, **40**, 1660 (1967); (d) P. F. D. Barnard, *J. Chem. Soc., A*, 2140 (1969).

[3] R. J. Balahura and R. B. Jordan, *J. Amer. Chem. Soc.*, **92**, 1533 (1970).

water and adding 5 *M* sodium hydroxide dropwise to a final pH of ~12. This solution was neutralized and subjected to ion exchange chromatography as described above and previously.[3] The usual treatment of the ion exchange resin with perchloric acid yields the perchlorate salt. However, analytical results always indicated that the product is a mixture of $((NH_3)_5CoNH_2COC_6H_5)(ClO_4)_3$ and $((NH_3)_5CoNHCOC_6H_5)(ClO_4)_2$. The unprotonated iodide salt has been isolated after many months of frustration with the perchlorate salt. Since no difficulties have been encountered with the iodide salt, it seems that crystal forces strongly favor the mixed perchlorate product. It should also be noted that the iodide salt of the unprotonated form may be isolated from the alkaline hydrolysis solution simply by addition of excess sodium iodide and cooling at −5° for 1-2 hr. The latter is a much more direct procedure and yields a product of analytical quality equal to that from the ion exchange procedure. It should be noted that the iodide salt shows evidence of iodine if stored at room temperature for several weeks, but has been stored in a refrigerator with no evidence of decomposition.

Because of difficulties in preparing the perchlorate salt and possible oxidation of the iodide, the chloride salt was used in the determination of the acid dissociation constant of the carboxamido complex. The chloride salt was prepared by treating an aqueous solution of the perchlorate with tetraphenylarsonium chloride, then removing the tetraphenylarsonium perchlorate by filtration and adding hydrochloric acid, ethanol, and ether to precipitate the protonated chloride salt.

Anal. Calcd for $(NH_3)_5Co(3\text{-}NCC_6H_4OH)(ClO_4)_3$: C, 15.0; N, 15.0; H, 3.56. Found: C, 15.1; N, 15.1; H, 3.64. Calcd for $(NH_3)_5Co(4\text{-}NCC_6H_4OH)(ClO_4)_3$[4]: C, 15.0; N, 15.0; H, 3.56. Found: C, 14.8; N, 15.0; H, 3.46. Calcd for $(NH_3)_5Co(NCC_6H_5)(ClO_4)_3$: C, 15.4; N, 15.4; H, 3.66. Found: C, 15.32; N, 15.05; H, 3.71. Calcd for $((NH_3)_5CoNHCOC_6H_5)I_2 \cdot 2H_2O$: C, 15.16; N, 15.16; H, 4.51. Found: C, 15.43; N, 15.37; H, 4.51.

The infrared spectra of the nitrile complexes show a characteristic C≡N stretching vibration, with that of the free nitrile in parentheses, at 2280 (2235), 2280 (2240), and 2270 cm^{-1} (2230) for the 4-cyanophenol, 3-cyanophenol, and benzonitrile systems, respectively. No C≡N stretch is observed in the alkaline hydrolysis product of the benzonitrile complex but an absorption at 1660 cm^{-1} may be assigned to the C=O stretch expected for the benzamide product.

The nmr and electronic spectra of the various complexes are summarized in Tables I and II, respectively.

Table I. Nmr Spectra of Pentaamminecobalt(III) Complexes in DMSO-d_6[a]

Ligand	*trans*-NH_3	*cis*-NH_3	Others
4-Cyanophenol	6.59	6.17	C_6H_4, 2.09, 2.24, 2.87, 3.01; OH, 0.54
3-Cyanophenol[b]	6.59	6.14	C_6H_4, 2.42, 2.53, 2.63, 2.80
Benzonitrile	6.47	6.06	C_6H_5, 1.94, 2.05, 2.18, 2.21
$HNCOC_6H_5^-$ [c]	6.77	6.63	C_6H_5, 2.20, 2.53
$H_2NCOC_6H_5$[c,d]	6.72	6.58	C_6H_5, 2.27, 2.62

[a] All values are relative to the solvent peak at τ 7.48. [b] The OH peak could not be detected. [c] The –NH and –NH_2 peaks of the ligand could not be definitely assigned. [d] Produced by adding trifluoroacetic acid to a DMSO solution of the $HNCOC_6H_5$ complex. This form rearranges to the O-bonded isomer in DMSO over a period of ~24 hr at room temperature.

Table II. Electronic Spectra of Pentaamminecobalt(III) Complexes[9]

Ligand	Absorption maxima, nm (extinction coefficient, M^{-1} cm^{-1})		
4-Cyanophenol	473 (108)	295 (2.3 × 10^4)	
3-Cyanophenol	469 (80)	299 (2.8 × 10^3)	245[c]
Benzonitrile	469 (79)	330 (82)	233 (2.2 × 10^4)[d]
$NHCOC_6H_5^-$	485 (88.3)	345 (117)	235 (1.57 × 10^4)
$NH_2COC_6H_5$	477 (77.6)	342 (89.5)	
4-NH-$COC_6H_4O^{2-}$ [b]	493 (114)	276 (2.0 × 10^4)	
3-NH-$COC_6H_4O^{2-}$ [b]	487 (82)	206 (3.1 × 10^3)	

[a] All spectra are in aqueous solution unless otherwise noted. [b] Obtained by dissolving the nitrile in ~0.1 *M* NaOH. [c] Shoulder. [d] A shoulder is also observed at ~270 nm (2.6 × 10^3).

Table III. Kinetic Results for the Hydrolysis of Nitrile Complexes

Nitrile	Temp, °C	$[OH^-]$, *M*	k_{obsd}, sec^{-1}	*k*, M^{-1} sec^{-1}
4-Cyanophenoxide	29	0.30	0.067	0.233
	29	0.40	0.097	0.243
	29	0.50	0.121	0.242
	34	0.20	0.076	0.380
	34	0.30	0.113	0.377
	34	0.40	0.159	0.398
	34	0.50	0.192	0.384
	40	0.20	0.125	0.625
	40	0.30	0.189	0.630
	40	0.40	0.267	0.668
	40	0.50	0.315	0.630
3-Cyanophenoxide	29	0.0125	0.030	4.80
	29	0.050	0.213	4.26
	29	0.075	0.380	5.07
	29	0.10	0.482	4.82
	29	0.20	0.996	4.98
	29	0.30	1.40	4.67
	35	0.075	0.52	6.93
	35	0.15	1.12	7.47
	35	0.30	2.20	7.33
	35	0.40	3.04	7.60
	40	0.075	0.919	12.3
	40	0.20	2.50	12.5
	40	0.30	3.62	12.1
	40	0.40	4.92	12.3
Benzonitrile	25.6	0.05	0.901	18.0
	25.6	0.125	2.38	19.0
	25.6	0.250	4.75	19.0
	40.4	0.05	3.53	70.5
	40.4	0.15	11.6	77.5

Kinetic Measurements. The alkaline hydrolysis of the coordinated nitriles was studied on an Aminco Morrow stopped-flow system equipped with a standard water circulating temperature control system. The increase in absorbance was observed at 420 nm for the 3- and 4-cyanophenol complexes and at 360 nm for the benzonitrile complex. A solution containing sodium hydroxide at the required concentration was mixed with a solution containing the cobalt(III)–nitrile complex and sodium perchlorate at a concentration to give a final ionic strength of 1.0 *M*. At each hydroxide ion concentration, between eight and ten traces of the transmittance change were recorded photographically, and the rate constants reported are the averages of these traces. The temperature was controlled by a standard water circulation system with the thermistor probe of the temperature controller in contact with the block containing the drive syringes. The temperature of the solutions in the drive syringes was measured with a copper–constantan thermocouple.

Determination of Acid Dissociation Constant. The pK_a was determined spectrophotometrically at 348 nm by adding known volumes of 1.0 *M* hydrochloric acid to a solution of the chloride salt of the benzamide complex in 14 ml of 1.0 *M* $LiClO_4$. The data were treated in a similar manner to that used previously for carbamatopentaamminecobalt(III).[5]

Results and Discussion

Before discussing the kinetic results it seems appropriate to consider the evidence that the alkaline hydroly-

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(4) This compound was first prepared and characterized by R. J. Balahura, Ph.D. Thesis, University of Alberta, 1971.

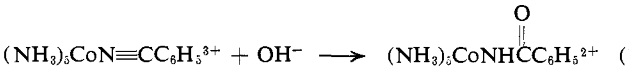
(5) R. J. Balahura and R. B. Jordan, *J. Amer. Chem. Soc.*, **93**, 625 (1971).

Table IV. Summary of Kinetic Results for Alkaline Hydrolysis of Nitriles

Compound	Rate constant, M^{-1} sec^{-1}, 25.6°	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, cal mol^{-1} deg^{-1}
$(NH_3)_5Co$(4-cyanophenoxide)$^{2+}$ [a]	0.18	16.3 ± 1.5	−7.4 ± 4
$(NH_3)_5Co$(3-cyanophenoxide)$^{2+}$ [a]	3.57	15.1 ± 1.5	−5.5 ± 4
$(NH_3)_5Co$(benzonitrile)$^{3+}$ [a]	18.8	16.5	2.7
Benzonitrile[b]	8.2×10^{-6}	19.9	−15.2
p-Chlorobenzonitrile[b]	7.2×10^{-6}	17.4	−19.3
Ni(2-cyano-1,10-phenanthroline)$^{2+}$ [c]	2.4×10^{4}	15.1	14
2-Cyano-1,10-phenanthroline[c]	2.6×10^{-3}	15.7	−20
Ni(2-cyanopyridine)$^{2+}$ [d]	6.3×10^{7}	13.7	23

[a] This work in NaOH-$NaClO_4$ at $\mu = 1.0$ *M*. [b] Reference 5, in 50% aqueous acetone. In calculating the rate constants at 25.6° it was found that Wiberg's results are better reproduced by the $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ given here. [c] Reference 1. [d] Reference 8.

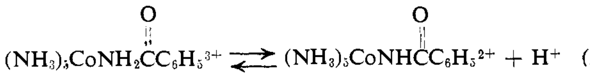
sis reaction proceeds according to



$$(NH_3)_5CoN\equiv CC_6H_5^{3+} + OH^- \longrightarrow (NH_3)_5CoNH\overset{\overset{O}{\|}}{C}C_6H_5^{2+} \qquad (1)$$

The product from the benzonitrile complex has been isolated and the chemical analysis and nmr spectrum are as expected for an N-bonded benzamido complex. The infrared spectrum of the product also shows that the $-C\equiv N$ stretching mode has been lost, consistent with the formation of the carboxamido product.

The product is also expected to undergo an acid-base reaction (eq 2) analogous to that found for the



$$(NH_3)_5CoNH_2\overset{\overset{O}{\|}}{C}C_6H_5^{3+} \rightleftharpoons (NH_3)_5CoNH\overset{\overset{O}{\|}}{C}C_6H_5^{2+} + H^+ \qquad (2)$$

N-bonded formamide complex.[3] The measured pK_a of 1.65 (25°, 1 *M* $LiClO_4$) for reaction 2 is smaller than that for the formamido complex, possibly due to stabilization of the conjugate base by conjugation with the benzene ring.

The similarity of the shifts in the visible spectra on hydrolysis of the cyanophenol and benzonitrile systems indicates that the former are also producing the N-bonded carboxamido product. The limited amount of nitrile complex prevented characterization of the hydrolysis product in the cyanophenol system.

The hydrolysis rate of all three complexes is described by the equation

$$-\frac{d\ln[\text{complex}]}{dt} = k_{\text{obsd}} = k_1[OH^-] \qquad (3)$$

The kinetic results are given in Table III. These results with the appropriate activation parameters are summarized in Table IV. Results from some previous studies are also given in Table IV for comparison.

It is apparent from Table IV that coordination to $(NH_3)_5Co^{3+}$ increases the rate of benzonitrile hydrolysis by a factor of 2×10^6. The hydrolysis of 4-cyanophenol has been studied by Cohen and Jones, but at 82° in 60% aqueous ethanol, and no realistic comparisons can be made for this system. It has been found previously[6,7] that nitrile hydrolysis rate constants show a linear free-energy relationship. This is also true for the coordinated nitriles studied here for which, at 25.6°

$$\log k = 3.89\sigma + 1.25 \qquad (4)$$

The σ values[8] of −0.52, −0.19, and 0 have been used for para and meta O^- and -H substituents, respectively.

The rate enhancement of 2×10^6 is of a similar magnitude to the value of 10^7 observed by Breslow, *et al.*,[1] for the nickel(II)-2-cyano-1,10-phenanthroline system. It must be remembered, however, that the two cases are different in that the nitrile is not bound initially to the metal in the latter while it is in the former system. The kinetic parameters for the catalysis are somewhat different in that $(NH_3)_5Co^{3+}$ appears to give both a more favorable $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, while with nickel(II)[1,9] only $\Delta S^{\ddagger}$ is affected significantly. This difference is at least qualitatively consistent with the argument of Breslow, *et al.*,[1] that the more favorable $\Delta S^{\ddagger}$ with nickel(II) is associated with bonding of the developing imino ion to the metal. In the system studied here the imino group is already bonded to cobalt(III).

Acknowledgment. The authors wish to acknowledge the financial support of the National Research Council of Canada.

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[6] K. B. Wiberg, *J. Amer. Chem. Soc.*, 77, 2519 (1955).

[7] L. A. Cohen and W. M. Jones, *ibid.*, **84**, 1626 (1962). The σ value for $-O^-$ used in this work is not consistent with current values (ref 8) and the cyanophenol system does not fit on a linear free-energy plot if current values are used.

[8] C. D. Ritchie and W. F. Sager, *Progr. Phys. Org. Chem.*, **2**, 323 (1964).

[9] R. Breslow and M. Schmir, *J. Amer. Chem. Soc.*, **93**, 4960 (1971).