Occurrence of Neighboring Group Participation Reactions in Amide-*N* and Amidine Complexes Derived from Pentaammine(dinitrile)cobalt(III) Ions

Patricia M. Angus and W. Gregory Jackson*

Department of Chemistry, University College, University of New South Wales, Australian Defence Force Academy, Canberra, ACT, Australia 2600

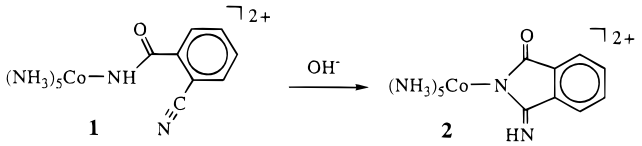
Received January 11, 1996[⊗]

N-Bonded pentaamminecobalt(III) complexes of 2-cyanobenzamide, 2-cyanoacetamide, and fumaric, succinic, glutaric, and adipic amide−nitriles have been prepared. The kinetics of the base hydrolysis of (succinonitrile)-pentaamminecobalt(III) have been measured: $k_{obsd} = k_{OH}$ [OH$^-$]; $k_{OH} = 1.23 \times 10^3$ {$I = 1.00$ M ($NaCH_3COO$), 25 °C}. Amido-*N*-coordinated 2-cyanobenzamide cyclized in aqueous base, and it forms [(1-oxo-3-iminoisoindolino-*endo*-*N*)pentaamminecobalt(III). In aqueous acid it protonates on the exo-imine and solvolyzes ($k_H = 7.9 \times 10^{-5}$ s^{-1}), forming the pentaammineaquacobalt(III) complex and 1-oxo-3-iminoisoindoline. In aqueous acid the amido-*N* complexes are protonated on the amide oxygen. The 2-cyanobenzamide species rearranges to form the nitrile-bonded linkage isomer in aqueous acid and also in Me_2SO-d_6, while the succinic amide nitrile complex rearranges more slowly in aqueous acid to form solely the nitrile-bonded linkage isomer. The kinetics of the reaction were $k_{obsd} = f(k_H[H^+]/(K_a + [H^+]))$ where $k_H = 3.4 \times 10^{-4}$ M^{-1} s^{-1} and $K_a = 6.76 \times 10^{-2}$ M, pK_a 1.2; pK_a 1.3 (spectrophotometric) {$I = 1.00$ M ($LiClO_4 \cdot 3H_2O$), 25 °C}. In Me_2SO-d_6 this amide-*N* complex reacts by three pathways: solvolysis, amide-*N* to -*O* isomerization, and amide-*N* to nitrile-bonded rearrangement (10%). The conjugate acid of the 2-cyanoacetamido-*N* complex reacted in both aqueous acid and acidified Me_2SO-d_6 by solvolysis, amide N to O isomerization, and amide-*N* to nitrile-bonded rearrangement (17% in each solvent). The fumaric, glutaric, and adipic amide−nitrile complexes bonded through the amide nitrogen react only by solvolysis and amide-*N* to -*O* isomerization. Pentaamminecobalt(III) complexes of 2-cyanobenzamidine and succinic, glutaric, and adipic amidine−nitriles bonded through the amidine secondary nitrogen have been prepared. The 2-cyanobenzamidine complex undergoes rapid ligand cyclization to form the corresponding complex of 1,3-diiminoisoindoline bonded through the deprotonated endocyclic nitrogen. In aqueous acid the complex is protonated on one of the exo-imines, and this solvolyzes to form the pentaammineaquacobalt(III) complex and 1,3-diiminoisoindoline {$k_H = 1.7 \times 10^{-3}$ s^{-1} (0.5 M HCl, 25 °C). Coordinated succinic amidine−nitrile also cyclizes in liquid ammonia to yield the complex of 2,5-diiminopyrrolidine bonded through the deprotonated endocyclic nitrogen. This is stable in aqueous base but solvolyzes rapidly ($t_{1/2}$ (s)) in aqueous acid to the aqua complex and succinimide; the latter is formed by hydrolysis of the free 2,5-diiminopyrrolidine. The dinuclear complex μ-decaammine(succinonitrile)dicobalt(III) was synthesized; in aqueous base it forms μ-(succinamido-*N*)-decaamminecobalt(III). The dinuclear dinitrile complex reacts in liquid ammonia to form the corresponding succinic amidine−nitrile species which cyclizes rapidly to form μ-decaammine(2,5-diiminopyrrolidino)cobalt(III) in which the ligand is bonded to cobalt(III) through the exo-imines.

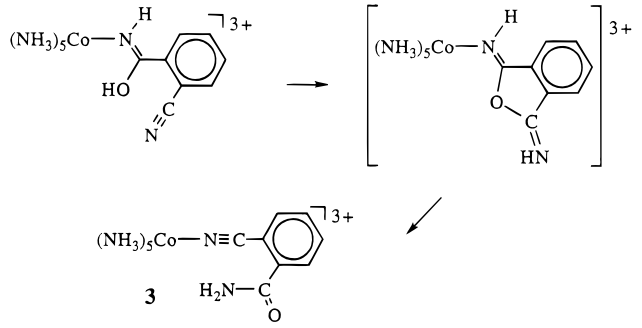
Introduction

Studies of some pentaammine(dinitrile)cobalt(III) complexes have shown that in aqueous base only the coordinated nitrile group hydrolyzes to an amide group, and in the resulting complex the organic ligand is bonded to the metal ion through the amide nitrogen and contains a remote nitrile group.[1,2] In this manner, base hydrolysis of pentaammine(1,2-dicyanobenzene)cobalt(III) produces a complex of 2-cyanobenzamide bonded through the deprotonated amide nitrogen (**1**), which subsequently undergoes ligand cyclization in aqueous base and forms the corresponding complex of 1-oxo-3-iminoisoindoline bonded through the endocyclic nitrogen[3,4] (**2**).[3]

In aqueous acid the 2-cyanobenzamide complex **1** is protonated and rearranges rapidly to form the nitrile-bonded linkage isomer **3**. The proposed mechanism,[3] which has been recently confirmed,[5] involves ligand cyclization with subsequent ring opening.



1 **2**



3

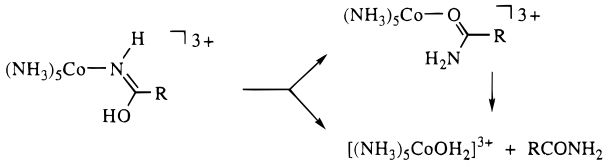
Ligand cyclization reactions have been encountered frequently in coordination chemistry.[6] This type of neighboring group

[⊗] Abstract published in *Advance ACS Abstracts*, October 1, 1996.

(1) Balahura, R. J. *Can. J. Chem.* **1974**, *52*, 1762−1773.
(2) Creaser, I. I.; Harrowfield, J. M. B.; Keene, F. R.; Sargeson, A. M. *J. Am. Chem. Soc.* **1981**, *103*, 3559−3564.
(3) Balahura, R. J.; Purcell, W. L. *Inorg. Chem.* **1979**, *18*, 937−941.
(4) Balahura, R. J.; Purcell, W. L. *Inorg. Chim. Acta* **1978**, *31*, L383−L384.

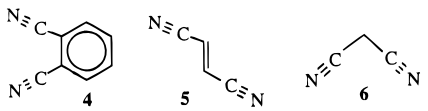
S0020-1669(96)00032-8 CCC: $12.00

participation does not involve the metal ion directly, although the latter may enhance the reactivity of functional groups. We have prepared a number of amido-*N* complexes bearing a remote nitrile group to investigate the occurrence of ligand cyclization reactions in such compounds. The amide-*N* to nitrile-bonded rearrangement in particular contrasts with the known reactivity of peptide[7] and simple amide-*N*[8,9] complexes, which rearrange in acid solution to form their oxygen-bonded isomers. The factors controlling the competitiveness of *N*- to *O*-bonded amide rearrangement vis-a-vis ligand cyclization are therefore of interest.



Some dinitriles are known to form cyclic imidines by reacting with ammonia at elevated temperature and pressure.[10−12] These reactions are further examples of neighboring group participation, and we determined whether they occurred with coordinated dinitriles under mild conditions.

Pentaamminecobalt(III) complexes of phthalonitrile (1,2-dicyanobenzene) (**4**),[1] fumaronitrile (**5**),[13] malononitrile (**6**),[2] succinonitrile (**7**),[14] glutaronitrile (**8**), and adiponitrile (**9**)[15] were used. In the first two, the functional groups are fixed in their



N≡C—$(CH_2)_n$—C≡N

7 n=2, **8** n=3, **9** n=4

orientation to each other, *cis* and *trans*, respectively, and in the malononitrile species the distance between the functional groups is invariant. The remaining dinitriles differ in the distance between the functional groups, which are separated by two methylene groups in succinonitrile and four in adiponitrile. In these complexes, rotation about the carbon−carbon bonds of the ligand gives rise to a number of conformations, only some of which are favorable for cyclization reactions. Complexes of fumaronitrile and the derived amide−nitrile were prepared to investigate the electronic effects of the remote functional group in a bifunctional complex that is rigid and where neighboring group participation is precluded. It should be noted that rearrangement to the (*Z*)-isomers is not likely as the (*E*)-isomers (fumaro) are the thermodynamically more stable forms.[16]

Table 1. Pseudo-First-Order Rate Constants for the Base Hydrolysis of Dinitrilepentaamminecocbalt(III) Complexes and Related Mononitrile Complexes in Aqueous Solution at 25 °C, I = 1.0

nitirle	k_{OH}/M^{-1} s^{-1}	nitrile	k_{OH}/M^{-1} s^{-1}
benzonitrile[a]	18.8	acetonitrile[d]	3.40
1,2-dicyanobenzene[b]	1.05×10^3	malononitrile[c]	5×10^5
acrylonitrile[c]	35.2	succinonitrile	1.23×10^3
fumaronitrile	$>10^4$		

[a] Pinnell, D.; Wright, G. B.; Jordan, R. B. *J. Am. Chem. Soc.* **1972**, *94*, 6104−6106. [b] Balahura, R. J.; Purcell, W. C. *Inorg. Chem.* **1981**, *20*, 4159−4163. [c] Creaser, I. I.; Harrowfield, J. MacB.; Keene, F. R.; Sargeson, A. M. *J. Am. Chem. Soc.* **1981**, *103*, 3559−3564. [d] Buckingham, D. A.; Keene, F. R.; Sargeson, A. M. *Inorg. Chem.* **1973**, *95*, 5649−5652.

Results

The pentaammine(dinitrile)cobalt(III) complexes were synthesized by a published method;[13] they were crystallized as their yellow perchlorate salts and characterized by microanalysis and ^{1}H and ^{13}C NMR, IR, and UV-vis spectroscopies. The ^{1}H NMR spectra showed that the complexes were free from pentaammineaquacobalt(III), while the ^{13}C NMR and the IR spectra showed separate signals for the coordinated and remote nitrile groups. A dinuclear cobalt(III) μ-decaammine(succinonitrile) complex was prepared by reacting succinonitrile with a large molar excess of pentaamminetriflatocobalt(III) complex. It was identified by NMR spectra, by its elution characteristics as a highly charged species on a cation exchange resin, and by microanalysis.

Syntheses and Structure of the Amide-*N*-Bonded Amide−Nitrile and Derivative Complexes. Base hydrolysis of the dinitrile complexes produced the amido-*N*-bonded amide−nitrile complexes in good yield.[1,2] They were crystallized as their pink-orange perchlorate salts and were characterized as above. In all cases the remote nitrile group was unaffected by aqueous base, and the IR and ^{13}C NMR spectra showed signals very close in frequency to those of the corresponding uncoordinated dinitrile. The presence of the N-bonded amido group was shown by the single amide proton signal at $\delta = 4.5-5.0$ ppm in the ^{1}H NMR spectrum and the ^{13}C NMR signal at $\delta = 170-180$ ppm in dimethyl sulfoxide. The coupling constants for the olefin protons in the fumaric amide−nitrile complex were identical with those of the fumaronitrile species, indicating no stereochemical change.[17] The rates of base hydrolysis were measured at pH 9−10 for the succinonitrile complex, but the rate for the fumaronitrile complex was too rapid to measure by conventional spectrophotometric techniques. We have at this stage been unable to determine the rate constants for base hydrolysis of the glutaronitrile and adiponitrile complexes as the kinetics are not straightforward. The rate constant is listed in Table 1 along with other relevant published data including those for comparable monofunctional complexes. The new kinetic data are listed in Table 2 (supporting information). For the succinonitrile complex, base hydrolysis at high pH was accompanied by some reductive decomposition arising from deprotonation at the α-methylene group, a reaction first observed for the malono-

(5) Angus, P. M.; Jackson, W. G. *Inorg. Chem.* **1994,** *33*, 1569−1571.
(6) Buckingham, D. A.; Davis, C. E.; Sargeson, A. M. *J. Am. Chem. Soc.* **1970**, *92*, 6159−6170.
(7) Paniago, E. G.; Margerum, D. W. *J. Am. Chem. Soc.* **1972**, *94*, 6704−6710.
(8) Angel, R. L.; Fairlie, D. P.; Jackson, W. G. *Inorg. Chem.* **1990**, *29*, 20−28.
(9) Fairlie, D. P.; Angus, P. M.; Fenn, M. D.; Jackson, W. G. *Inorg. Chem.* **1991**, *30* 1564−1569.
(10) Elvidge, J. A.; Linstead, R. P. *J. Chem. Soc.* **1952**, 5000−5007.
(11) Elvidge, J. A.; Linstead, R. P. *J. Chem. Soc.* **1954**, 442−448.
(12) Elvidge, J. A.; Linstead, R. P.; Salaman, A. M. *J. Chem. Soc.* **1959**, 208−215.
(13) Kupferschmidt, W. C.; Jordan, R. B. *Inorg. Chem.* **1982**, *21*, 2089−2091.
(14) Kupferschmidt, W. C.; Jordan, R. B. *Inorg. Chem.* **1981**, *20*, 3469−3473.
(15) Butler, D. G.; Creaser, I. I.; Dyke, S. F.; Sargeson, A. M. *Acta Chem. Scan.* **1978**, *A32*, 789−797.
(16) Coffey, S., Ed. Rodd's Chemistry of Carbon Compounds, 2nd ed.; Elsevier: Amsterdam, 1965; Vol. I, Part D, pp 338−345.
(17) Gaudemer, A. Determination of Relative Configuration by NMR Spectroscopy. In *Stereochemistry. Fundamentals and Methods*; Kagan, H. B., Ed.; Georg Thieme: Stuttgart, 1977; Vol. 1, pp 44−50.

nitrile complex.[2] In the aromatic and olefin systems, the rate constants of the dinitrile complexes are greater by two or more orders of magnitude compared with the appropriate mononitrile complexes. In the saturated dinitriles, substitution *gem* to the coordinated functional group increased the rate constant by 10^5 in comparison with the acetonitrile complex, and substitution at the methylene group *vicinal* to the coordinated functional group increased it only by 10^3.

The dinuclear succinonitrile complex produced the corresponding dinuclear diamido complex when dissolved in aqueous base. The NMR spectra showed a symmetrical species consistent with this. Attempts to isolate the dinuclear amido−nitrile complex by adding less than 1 equiv of base were unsuccessful; the products were the diamido and the dinitrile complexes and no other Co(III) species. Clearly the rate of hydrolysis of the second coordinated nitrile is significantly greater than that of the first.

Reactions of the Amido-*N* Species. These complexes are unreactive in aqueous base save for the 2-cyanoacetamide complex, which slowly decomposes to Co(II) via deprotonation at the methylene group, and the 2-cyanobenzamide complex in which the organic ligand cyclizes to form 1-oxo-3-iminoisoindoline bonded through the deprotonated endocyclic nitrogen as previously reported.[3,4] The latter complex is stable indefinitely in aqueous base and was crystallized from acid solution.[3] The ^{1}H NMR spectrum of this species {pentaammine(1-oxo-3-iminoisoindoline)cobalt(III)} in Me_2SO-d_6 clearly showed two inequivalent NH protons at 8.71 and 10.53 ppm. In aqueous solution this protonation reaction is initially reversible, but the protonated species solvolyzes slowly ($k_H = 7.9 \times 10^{-5}$ s^{-1}), and the products were identified by ^{1}H and ^{13}C NMR spectroscopies as the pentaammineaqua complex and free phthalimide. Alternative mechanisms can be postulated: that the imine is hydrolyzed and the resulting N-bonded phthalimide complex solvolyzes or that the 1-oxo-3-iminoisoindoline complex solvolyzes and the free ligand is subsequently hydrolyzed to phthalimide. It would appear that the latter mechanism is the correct one since pentaammine(phthalimido-*N*)cobalt(III) has been synthesized as part of another study and it is indefinitely stable in acid solution.[18] The acid hydrolysis of 1-oxo-3-iminoisoindoline to phthalimide is a known reaction.[10]

All the amido-*N* complexes are reactive in aqueous acid. The initial reaction is protonation of the coordinated amide group, and the yellow amide-*N* complexes were crystallized and characterized in all cases except for the 2-cyanobenzamide complex, which rearranges too quickly for this species to be observed in deuterated water or dimethylsulfoxide.[3] The amide-*N* complexes were allowed to react in aqueous acid, and the products were isolated by ion exchange chromatography and characterized by IR, ^{1}H, and ^{13}C NMR spectroscopies. The succinic amide−nitrile complex rearranges completely to form a single yellow species, the ^{1}H NMR spectrum of which clearly shows two broad signals at 7.12 and 7.57 ppm characteristic of the diastereotopic protons of an uncoordinated amide group,[19] while the IR nitrile stretching frequency is at 2320 cm^{-1} and the ^{13}C NMR nitrile signal is at 133.0 ppm, comparable with the coordinated nitrile signals for the pentaammine(succinonitrile)cobalt(III) complex. This complex is the nitrile-bonded linkage isomer. The kinetics of the reaction in aqueous acid, I = 1.00 M ($LiClO_4 \cdot 3H_2O$), 25 °C, were investigated, and the rate law is

$$k_{obsd} = \frac{k_H[H^+]}{K_a + [H^+]}$$

where $k_H = 3.4 \times 10^{-4}$ M^{-1} s^{-1} and $K_a = 6.76 \times 10^{-2}$, p$K_a$ 1.2. The pK_a of the coordinated amide group was also determined spectrophotometrically as 1.3. The variation of k_{obsd} with [H$^+$] is shown in Figure 1. The kinetic data are listed in Table 3 (supporting information). This reaction is analogous to that of the 2-cyanobenzamide complex but is slower by a factor of 10^3.[3]

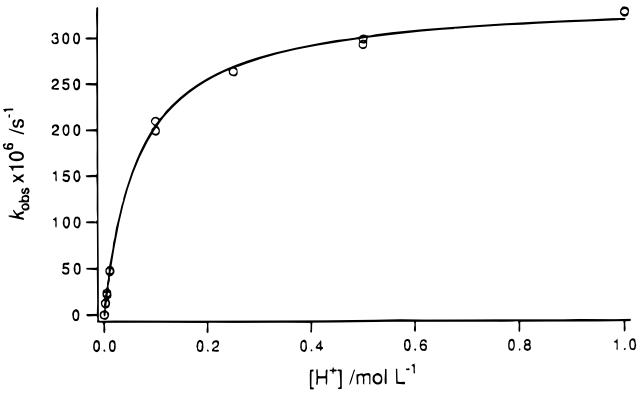


Figure 1. Graph showing the variation of the observed and calculated rate constants for the amide-*N* to nitrile-bonded rearrangement of $[(NH_3)_5CoNHC(OH)(CH_2)_2CN]^{3+}$ with [H$^+$] in aqueous solution, I = 1.00 M (LiClO4), 25 °C.

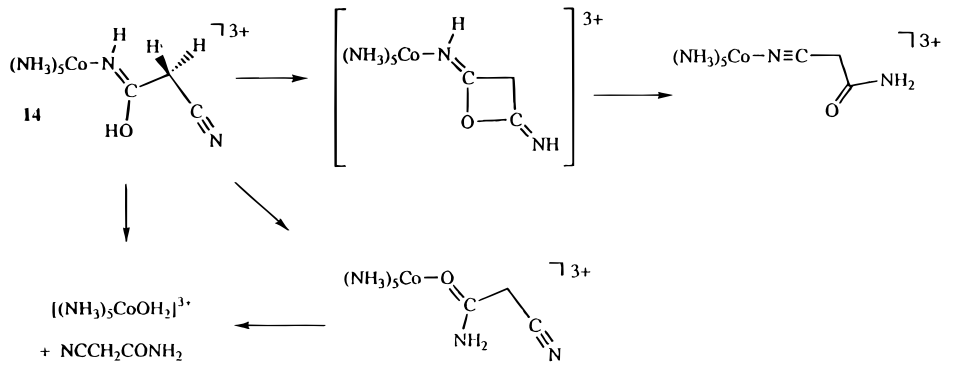
The 2-cyanoacetamide complex reacts quite slowly in aqueous acid (1 M); the reaction was quenched after 24 h to prevent significant solvolysis of any nitrile-bonded product. No attempt was made to determine the rate of disappearance of the amide−nitrile complex as the visible and ^{1}H NMR spectra showed that it is not fully protonated in acid solution and, as the reaction proceeded, more of the amide complex would deprotonate. The Co(III) products are the pentaammineaqua (83%) and the nitrile-bonded 2-cyanoacetamide (17%) complexes. The latter complex was characterized by its IR and ^{1}H and ^{13}C NMR spectra, and the identification was confirmed by preparation of the nitrile-bonded complex directly from 2-cyanoacetamide.[14] The two complexes were spectroscopically identical.

The glutaric, adipic, and fumaric amide−nitrile complexes (all bonded through the amide nitrogen) produce only pentaamineaquacobalt(III) when reacted in aqueous acid. We suggest that the pentaammineaqua complex produced in these reactions and the corresponding 2-cyanoacetamide complex arises, at least in part, from amide-*N* to amide-*O* rearrangement; this reaction in monodentate cobalt(III) complexes is accompanied by solvolysis, and the amide-*O* complexes produced by rearrangement solvolyze also.[8,9] Recently this reaction has been observed directly in aqueous solution for the N-bonded 2-pyridone complex,[20] but this is not usually the case in water as most amide-*O* complexes solvolyze more rapidly than they are formed during *N* to *O* rearrangement.

The amide-*N* complexes were also reacted in Me_2SO-d_6 acidified with triflic acid so that the rearrangements could be observed directly using ^{1}H NMR spectroscopy (the amide protons exchange in D_2O so it was not possible to monitor directly the rearrangements in aqueous media in this way). The reaction of the 2-cyanobenzamide complex in this solvent is quite analogous to that in water, and the formation of the nitrile-bonded isomer is too rapid to permit observation of the protonated amide intermediate. However the reaction of the fumaric amide−nitrile complex could be monitored easily by ^{1}H NMR spectroscopy. Five minutes after dissolution, 25% of the starting material had been consumed and the rate constant

(18) Angus, P. M.; Jackson, W. G. Manuscript in preparation.
(19) Stewart, W. E.; Siddall, T. H. *Chem. Rev.* **1970**, *70*, 517−551.
(20) Angus, P. M.; Jackson, W. G. *Inorg. Chem.* **1994**, *33*, 477−483.

Scheme 1



for its disappearance is 1×10^{-3} s^{-1}, which is greater than that in aqueous solution. Also two signals at 3.90 and 3.89 ppm had appeared in the spectrum and are characteristic of the *cis* ammine signals for the oxygen-bonded amide[21] and the solvento complexes,[22] respectively. After 50 min two broad signals at 8.1 and 9.6 ppm attributable to the diastereotopic NH_2 protons of an oxygen-bonded amide complex[21] were clearly visible. With time these signals disappeared because of solvolysis, and after 24 h the only signals in the spectrum were those due to the solvento complex and the free ligand.

Analogous spectra were recorded during the reactions of the glutaric and adipic amide−nitrile complexes in acidic Me_2SO-d_6, but these react more slowly. After 4 h the characteristic amide-*O* proton signals at 7.3 and 9.1 ppm[21] were clearly visible and the intensity of these peaks declined slowly thereafter as the amide-*O* complex solvolyzed. The only species detected during these reactions were the amide-*N*, amide-*O*, and solvento complexes and also the free ligands. Hence for the fumaric, glutaric, and adipic amide−nitrile complexes, only amide-*N* to -*O* rearrangement, with accompanying solvolysis, was observed; capture of the remote nitrile was not competitive.

The cyanoacetamide complex reacts comparatively rapidly in acidified Me_2SO-d_6 . After 2 min, solvento complex and cyanoacetamide were detected in the spectrum, which was complicated due to the overlapping methylene signals from the three species containing cyanoacetamide. The presence of the oxygen-bonded isomer was confirmed by the *cis* ammine peak at 3.98 ppm and the amide proton signals at 8.0 and 9.5 ppm. Within 10 min the *cis* ammine peak for the nitrile-bonded isomer was detected. After 45 min no starting material remained, and after 15 h the only cobalt(III) species present were solvento complex and the nitrile-bonded isomer (17%); the product ratio was the same in aqueous solution. The identification of the nitrile-bonded linkage isomer was confirmed by recording the ^{13}C NMR spectrum and observing the signal for the coordinated nitrile group at 128.6 ppm. The reactions of the 2-cyanoacetamide complex are summarized in Scheme 1 and show the competing linkage isomerization and solvolysis reactions of the amide-*N*-bonded complex.

For the succinic amide−nitrile complex however, the course of the reaction, as well as the rate, is different in Me_2SO-d_6 than in aqueous solution. The reaction products are the nitrile-bonded isomer, the solvento complex, and the amide-*O* isomer; the latter was identified in the ^{1}H NMR spectra by its *cis* amine signal at 4.0 ppm and its amide proton signals at 7.5 and 9.3 ppm. Ultimately only the nitrile-bonded isomer (10%), the solvento complex, and free ligand remain after solvolysis of the amide-*O* complex is complete. The rate constant for the disappearance of the amide-*N* complex was estimated as 6×10^{-4} s^{-1}, so the rate constant for the N to N rearrangement in Me_2SO-d_6 is 6×10^{-5} s^{-1}, about one-tenth of the rate in aqueous solution. Since the amide protons of the nitrile-bonded isomer and the free ligand exchange in acidic Me_2SO-d_6 and were not observed, the presence of that complex was confirmed by recording the ^{13}C NMR spectrum of the solution after a 12 h reaction and observing the coordinated nitrile signal at 133.0 ppm.

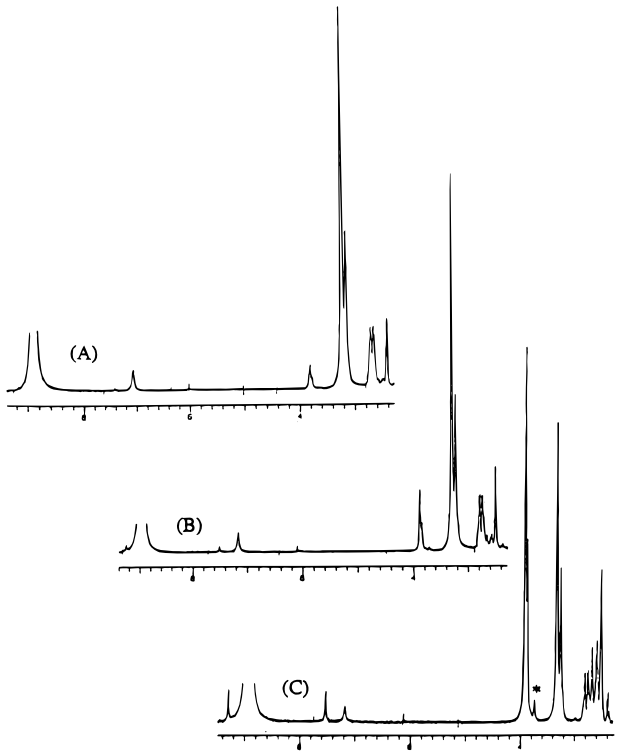
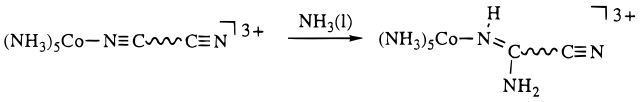


Figure 2. ^{1}H NMR spectra showing products of the reactions of $[(NH_3)_5CoNHC(OH)(CH_2)_2CN]^{3+}$ in Me_2SO-d_6/triflic acid (20 °C) at 2 min (A), 15 min (B), and 40 min (C).

A selection of the ^{1}H NMR spectra for the succinic amide−nitrile complex is shown in Figure 2, and the large peak at 9 ppm is acid/water. Spectrum A was recorded 2 min after dissolution and shows the peaks for the amide-N-bonded starting material and small peaks at 4.0 and 3.9 ppm, which are the *cis* ammines of the amide-*O* and solvento complexes, respectively. Spectrum B shows that after 15 min the concentration of the amide-*O* complex has increased and the broad, high-frequency signals of its amide protons can be seen at 9.3 and 7.5 ppm. In spectrum C, which was recorded after 40 min, the peak marked with an asterisk arises from the *cis* ammine of the nitrile-bonded isomer.

(21) Angus, P. M.; Fairlie, D. P.; Jackson, W. G. *Inorg. Chem.* **1993**, *32*, 450−459.
(22) Dixon, N. E.; Jackson, W. G.; Lancaster, M. J.; Lawrence, G. A.; Sargeson, A. M. *Inorg. Chem.* **1981**, *20*, 470−476.

Synthesis, Structure, and Reactions of Amidine-Bonded Amidine−Nitrile Complexes. The perchlorate salts of the dinitrile complexes were dissolved in liquid ammonia to aminate the coordinated nitrile group as shown:[23]



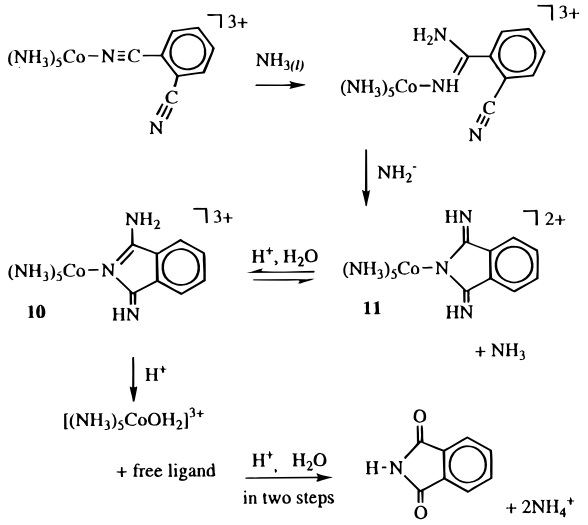
The fumaronitrile complex decomposes rapidly to cobalt oxides while the malononitrile complex is recovered unchanged after a 15 min reaction. The unreactivity of the latter complex is almost certainly due to deprotonation at the methylene group (pK_a 5.3 in water)[2], and the resulting species is not reactive toward nucleophiles. A lack of reaction, for a similar reason, has been observed for pentaammine(cyanamide)cobalt(III) in aqueous base.[24]

However, the succino-, glutaro- and adiponitrile complexes react rapidly in liquid ammonia producing an orange species; its ^{1}H NMR spectra in Me_2SO-d_6 showed signals at ∼5.5 ppm characteristic of monodentate amidine complexes.[23] The ^{13}C NMR spectra showed signals at 175 ppm for the coordinated amidine groups and also showed signals at 120 ppm characteristic of remote nitrile groups. In the IR spectra the nitrile stretching vibrations were found at 2250 cm^{-1}, characteristic of uncoordinated nitriles. We conclude that only the coordinated nitrile groups are converted to amidines while the remote nitriles are unaffected.

The phthalonitrile complex also reacts rapidly with liquid ammonia, but the product was a dark pink species whose perchlorate salt was only slightly soluble in water. The ^{1}H NMR spectrum of this compound implied that the unique ligand is bonded to the metal through an sp^2 nitrogen (*cis* NH_3 ≃ 3.8 ppm), and a signal at 8.39 ppm (2H) can be assigned as two nitrogen-bonded imine protons. The ^{13}C NMR spectrum showed that the unique ligand is symmetrical, only one functional group signal (at 172.9 ppm) and only three signals for the aromatic ring carbons were observed. The IR and ^{13}C NMR spectra did not reveal any nitrile signals. The spectral data are consistent with a complex of 1,3-diiminoisoindoline bonded through the deprotonated endocyclic nitrogen (**11**). It is likely that the complex was formed in two steps: first, the phthalonitrile complex reacts with ammonia to form the amidine-bonded 2-cyanobenzamidine complex and second, in the presence of excess ammonia, the deprotonated coordinated amidine group condenses with the remote nitrile group to form a cyclic imidine. Phthalonitrile also undergoes this reaction with ammonia, but high temperature and pressure are required.[10] Attempts to isolate the amidine-bonded intermediate by reacting the dinitrile complex in a solution of ammonium perchlorate in liquid ammonia were unsuccessful.

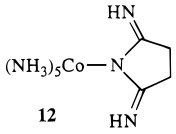
The diiminoisoindolino complex is stable in aqueous base, and it is also crystallizes from acid solution as the monoprotonated, orange species (**11**), which was isolated and characterized as the perchlorate salt. The NMR spectral data implied that the complex was protonated on one of the exoimines (the ^{1}H NMR spectrum shows three NH signals at 7.90, 9.75, and 10.65 ppm), while the ^{13}C NMR had two signals for the imine carbons and six for the aromatic ring carbons; such asymmetry implies that the proton resides on an exocyclic nitrogen. The complex solvolyzes fairly rapidly, $k_H = 1.7 \times 10^{-3}$ s^{-1} (0.5 M HCl, 25 °C), and the products are the

Scheme 2



pentaammineaqua complex and ultimately phthalimide. The heterocyclic imine groups are not hydrolyzed until the ligand has left the metal ion since the N-bonded phthalimide complex is quite stable in acid solution.[18] Acid hydrolysis of diiminoisoindoline to phthalimide with the stepwise liberation of ammonia is a known reaction.[11] The reactions of the phthalonitrile complex in liquid ammonia are summarized in Scheme 2.

When the succinonitrile complex was treated with liquid ammonia for 2 h, the product was a dark pink complex whose spectral data were consistent with the formation of another imidine complex, pentaammine(2,5-diiminopyrrolidino)-cobalt(III) (**12**). An analogous reaction occurs with succino-



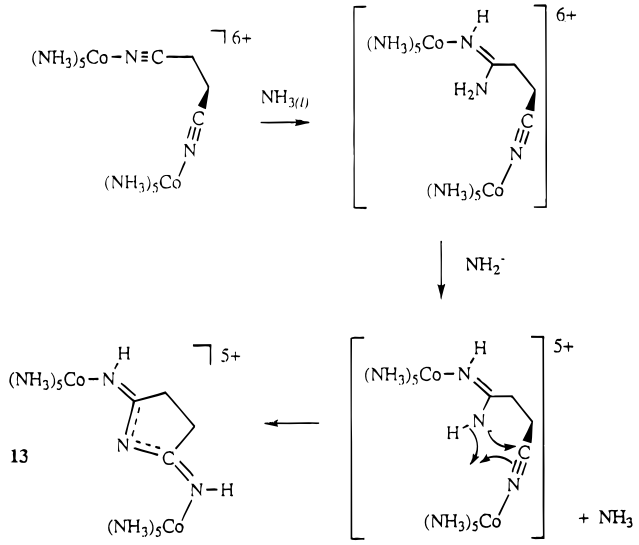
12

nitrile but under much more stringent conditions.[11] This imidine complex is also stable in aqueous base, but in acidic solution it solvolyzes very rapidly, producing the pentaammineaqua complex and succinimide. The ligand must be hydrolyzed after leaving the metal ion since it is known that the N-bonded succinimide complex solvolyzes very slowly ($t_{1/2}$ (days)) in acid solution.[25] The reactions of the succinonitrile complex are analogous to those of its aromatic analogue, which are shown in Scheme 2.

The dinuclear succinonitrile complex also reacts with liquid ammonia to form an orange species, the ^{13}C NMR spectrum of which showed that the unique ligand was a symmetrical species; only one signal was observed for the functional group (192.4 ppm) and only one for the methylene carbons (33.0 ppm). However, the functional groups are not monodentate amidines as their ^{13}C NMR signal occurs at ∼174 ppm. The high-frequency signal is consistent with a complex of a deprotonated pyrrolidine ring which is coordinated exo to the ring; examples are $[(NH_3)_5Co(\text{succinimido-}O)]^{2+}$ (C═O−Co and C═O, 203 and 194 ppm)[25] and $[(NH_3)_5Co(\text{2-oxo-5-iminopyrrolidino-}exo\text{-}N)]^{2+}$ (C═O and C═NHCo, 192.3 and 191.8).[18] All the spectra are consistent with this species being a dinuclear diiminopyrrolidino complex bonded through the exocyclic nitrogens and deprotonated at the ring nitrogen (**13**). We propose that it

(23) Fairlie, D. P.; Jackson, W. G. *Inorg. Chim. Acta* **1990**, *29*, 140−143.
(24) Dixon, N. E.; Fairlie, D. P.; Jackson, W. G.; Sargeson, A. M. *Inorg. Chem.* **1983**, *22*, 4038−4046.
(25) Angus, P. M.; Jackson, W. G. *Inorg. Chem.* **1991**, *30*, 4806−4813.

Scheme 3



is formed in a two-step reaction: first, the μ-dinitrile complex adds ammonia at one functional group to form a dinuclear amidine−nitrile complex; second, the uncoordinated nitrogen of the amidine group condenses intramolecularly with the remaining coordinated nitrile group to form an imidine complex bonded through both exocyclic nitrogens, rather than react intermolecularly with ammonia to form a diamidine (a reaction analogous to the latter is, however, preferred in aqueous base). The reactions are shown in Scheme 3. The complex is stable in aqueous base for a period of several hours and is not protonated in aqueous acid or in dimethylsulfoxide with added triflic acid.

The amidine complexes derived from glutaro- and adiponitrile were unreacted in liquid ammonia even after 3 h. In aqueous base they decomposed slowly to cobalt oxides. No evidence was found for cyclization reactions in those cases.

Discussion

Three reactions involving neighboring group participation have been identified in this series of amide-*N*- and amidine-bonded complexes derived from pentaammine(dinitrile)-cobalt(III) complexes. The first reaction was the cyclization of an amido-nitrile ligand to form a substituted heterocycle, and it was detected only with the 2-cyanobenzamide complex.[3,4] The second reaction was the amide-*N* to nitrile-bonded rearrangement which has been observed for the 2-cyanobenzamide, 2-cyanoacetamide, and succinic amide−nitrile complexes. Finally coordinated imidines were formed by the cyclization of three amidine-bonded complexes bearing remote nitrile groups; they were the 2-cyanobenzamidine and the monodentate and dinuclear succinic amidine−nitrile complexes. Two properties of the bifunctional ligands affected the reactivity of this series of complexes: the structure of the ligand and the electronic activation of a functional group, which may be due to coordination of the ligand by the metal ion and to the electronic effects of the electron-withdrawing nitrile group remote from the metal ion. If these properties did not favor the ligand cyclization reactions, then the presence of the remote nitrile group did not affect the reactivity of the complexes, and their reactions were similar to those of complexes with monofunctional ligands.

The activating effect of coordination on the nitrile group is well-known[26,27] while coordination also increases the acidity of the amidine group.[23] Conversely coordination of a deprotonated amide through nitrogen does not activate that functional group toward nucleophilic attack,[28] but electron-withdrawing substituents do activate coordinated amide-*N* complexes toward amide-*N* to -*O* rearrangement.[9] The degree of electronic activation by the remote nitrile groups can be gauged by comparing the rates of base hydrolysis of the dinitrile complexes with that of their monofunctional analogues (Table 1). Dinitrile complexes showing significant activation were the malononitrile, fumaronitrile, phthalonitrile, and succinonitrile species.

2-Cyanobenzamide and 2-cyanobenzamidine have almost planar structures, and the two functional groups are in close proximity due to geometry and conjugation. Also, the products of their intramolecular cyclization reactions are five-membered rings, which are geometrically favored. Consequently, cyclization reactions of their complexes were rapid, as expected, because the conditions are optimized both geometrically and electronically.

2-Cyanoacetamide has considerable electronic activation because the functional groups are *gem* to each other, but its geometry is not quite as favorable for cyclization reactions as that of 2-cyanobenzamide. First, the amide-*N* to nitrile-bonded rearrangement involves the formation of a four-membered ring as a rate-determining step, and the angle strain in such a ring means that the enthalpy change for its formation is less favorable.[29] Second, rotation about the $C_{methylene}-C_{amide}$ bond can give rise to three conformers, only one of which will be suitable for the cyclization reaction. The reactive conformer (**14**, Scheme 1) has the amide oxygen pointing toward the nitrile group, and the amide group is almost coplanar with it. This is the conformation adopted by 2-cyanoacetamide in the solid state,[30] and studies on 2-chloro-*N*-methylacetamide (a rather similar structure) have shown that this conformer is as stable as the other two in the liquid state.[31] Thus ring strain and the existence of unreactive conformers disfavor the amide-*N* to nitrile-bonded rearrangement in this case, so its rate is of the same order of magnitude as that for the amide-*N* to -*O* reaction. Here the relative rates do not vary significantly in water and deuterated dimethyl sulfoxide. The rate of amide-*N* to -*O* rearrangement is unaffected by the conformation of the ligand.

Succinonitrile derivatives have a more complex stereochemistry as rotation can occur about the $C_{amide}-CH_2$ and CH_2-CH_2 bonds. Studies with succinonitrile have shown that the two gauche conformers (arising from rotation about the CH_2-CH_2 bond) are the dominant species at room temperature,[32] and these are appropriately structured to undergo cyclization reactions. It seems likely that these conformers would be the more stable ones in succinic amide−nitrile and succinic amidine−nitrile. The existence of some unreactive conformers would certainly tend to disfavor the N to N rearrangement; however, cyclization reactions in these ligands produce five-membered rings which usually form rapidly,[33] and this, combined with electronic activation by the remote nitrile group in the case of pentaamminecobalt(III) complexes of succinic amide−nitrile and succinic amidine−nitrile, has provided sufficiently favorable conditions for the cyclization reactions to be observed. In the

(26) Buckingham, D. A.; Keene, F. R.; Sargeson, A. M. *J. Am. Chem. Soc.* **1973**, *95*, 5649−5652.
(27) Pinnell, D.; Wright, G. B.; Jordan, R. B. *J. Am. Chem. Soc.* **1972**, *94*, 6104−6106.
(28) Sigel, H.; Martin, R. B. *Chem. Rev.* **1982**, *82*, 385−426.
(29) Wiberg, K. B. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 312−322.
(30) Chieh, P. C.; Trotter, J. *J. Chem. Soc. A* **1970**, 184−187.
(31) Mizushima, S.-I.; Shimanouchi, T.; Ichishima, I.; Miyazawa, T.; Nakagawa, I.; Araki, T. *J. Am. Chem. Soc.* **1956**, *78*, 2038−2041.
(32) Kubota, M.; Schulze, S. R. *Inorg. Chem.* **1964**, *3*, 853−856.
(33) Cápon, B.; McManus, S. P. *Neighbouring Group Participation*; Plenum: New York, 1976; Vol. 1, pp 1−75.
(34) Matsubara, I. *J. Chem. Phys.* **1961**, *35*, 373−374.

case of the succinonitrile dimer, activation of both functional groups by coordination has led to a rapid cyclization reaction in liquid ammonia.

The cyclization reactions of the succinonitrile derivatives are slower than those of the aromatic complexes in the case of the *N* to *N* rearrangement by a factor of 10^3. This must be due to the existence of unreactive conformers in the case of the succinonitrile derivatives since the rates of base hydrolysis of the succinonitrile and phthalonitrile complexes are similar. The *N* to *N* reaction was monitored in deuterated dimethyl sulfoxide where it was less significant (one-tenth) than the amide-*N* to -*O* isomerization which was not detected in water. Changes in conformational equilibria, rates of proton transfer, and solvation differences could affect the relative rates of these reactions in different solvents. It is known that the relative rates of the amide-*N* to -*O* rearrangement and amide-*N* solvolysis vary according to solvents.[8]

No cyclization reactions were observed for the pentaamminecobalt(III) derivatives of glutaronitrile and adiponitrile, and this can be attributed to unfavorable structures in the difunctional ligands and little electronic activation by the remote nitrile group. The structure of glutaronitrile in the liquid state has been determined using IR spectroscopy; there are four posssible conformers arising from internal rotation about the carbon−carbon bonds. Only one of these conformers could participate in cyclization reactions and this species was not detected at room temperature.[35] At higher temperatures the conformational equilibrium would be different, which could explain the reaction of glutaronitrile and ammonia to form a cyclic imidine at 100 °C.[12]

Experimental Section

Spectra. UV-vis spectra were obtained with a Cary 210 spectrophotometer using quartz cells. IR spectra were measured on a JASCO A-100 spectrophotometer using Nujol mulls or liquid films where appropriate. ^{1}H and ^{13}C NMR spectra were obtained with a Varian XL 300 spectrometer with a probe temperature of 20 °C using Me_2SO-d_6 (Aldrich) as solvent.

Syntheses. Caution! Perchlorate salts are potentially explosive and should be handled cautiously and in small quantities. All complexes analyzed satisfactorily for H, C, and N. Fumaronitrile was prepared by a published method.[35] The dinitrile complexes were synthesized from $[Co(NH_3)_5OSO_2CF_3](CF_3SO_3)_2$[22] ("triflato complex"), and the free ligand using the general method of Kupferschmidt and Jordan.[13]

$[(NH_3)_5CoNCCH_2CN](ClO_4)_3$. Freshly distilled malononitrile (40 g, Aldrich), triflato complex (12 g), and triflic acid (0.5 mL) were heated in a sealed flask at 70 °C for 1 h. The products were precipitated in ether, taken up in acidified water (pH 4, CH_3COOH), and then rapidly crystallized and recrystallized with 6 M $HClO_4$. The bright yellow crystals were washed with ethanol and ether and air-dried (6.0 g, 57%). Visible (M^{-1} cm^{-1}, 0.10 M $HClO_4$): ϵ_{466} 64, ϵ_{332} 63 (*cf.* ϵ_{467} 62.9, ϵ_{334} 63.6;[14] ϵ_{474} 72, ϵ_{341} 82;[2] and ϵ_{465} 84[37]). IR (cm^{-1}): nitrile stretch 2340 (coord.), 2270 (remote) (*cf.* 2270 for free malononitrile). ^{1}H NMR (δ, ppm): 4.94, CH_2; 3.38, *trans* NH_3; 3.78, *cis* NH_3. ^{13}C NMR (δ, ppm): 11.3, CH_2; 110.8, C≡N free; 123.8, C≡N coord.

$[Co(NH_3)_5NC(CH_2)_3CN](ClO_4)_3$. IR ($cm^{-1}$): nitrile stretch 2330 (coord.), 2260 (remote) (*cf.* 2260 for free glutaronitrile). Visible (0.1 M $HClO_4$, M^{-1} cm^{-1}): ϵ_{465} 63.0, ϵ_{332} 57.0. ^{1}H NMR (δ, ppm): 1.98 (2H, m) CH^{β}_2; 2.67 (2H, m), CH^{γ}_2; 3.02 (2H, m), CH^{α}_2; 3.29, *trans* NH_3; 3.72, *cis* NH_3. ^{13}C NMR (δ, ppm): 15.2, $C^{\gamma}H_2$; 17.4, $C^{\alpha}H_2$; 20.2, $C^{\beta}H_2$; 119.5, C≡N free; 131.6, C≡N coord.

$[Co(NH_3)_5NC(CH_2)_4CN](ClO_4)_3$. IR ($cm^{-1}$): nitrile stretch 2290 (coord.), 2240 (remote) (*cf.* 2240 for free adiponitrile). Visible (0.1 M $HClO_4$, M^{-1} cm^{-1}): ϵ_{465} 64.0, ϵ_{332} 55.5. ^{1}H NMR spectrum (δ, ppm): 1.69 (4H, m), $CH^{\beta}_2CH^{\gamma}_2$; 2.53 (2H, m), CH^{δ}_2; 2.95 (2H, m), CH^{α}_2; 3.29, *trans* NH_3; 3.71, *cis* NH_3. ^{13}C NMR (δ, ppm): 15.0, $C^{\omega}H_2$; 17.0, $C^{\alpha}H_2$; 22.6, $C^{\gamma}H_2$; 22.9, $C^{\beta}H_2$;119.8, C≡N free; 132.0, C≡N coord.

$[(NH_3)_5Co(NCC_6H_4\text{-}2\text{-}CN)](ClO_4)_3\cdot H_2O$. Phthalonitrile (Fluka, 5.0 g) and triflato complex (3.0 g) were heated in sulfolane (30 mL) and acidified with 2 drops of triflic acid in a sealed flask at 60 °C for 1 h. The crude product was precipitated in AnalaR ether (300 mL) and recrystallized twice from acidified water/acetone (80:20) with concentrated $NaClO_4$ solution. The acetone prevents the product from crystallizing with sulfolane, which in its absence has been repeatedly observed. The pale yellow complex was washed with ethanol and ether, and air-dried (0.85 g, 29%). IR (cm^{-1}): nitrile stretch 2300 (coord.), 2240 (remote) (*cf.* 2240 for free phthalonitrile). Visible (0.1 M $HClO_4$, M^{-1} cm^{-1}) ϵ_{466} 67.5 (*cf.* ϵ_{466} 66[3]). ^{1}H NMR (δ, ppm): 8.25, 8.35 (aromatic); 3.49, *trans* NH_3; 3.88, *cis* NH_3. ^{13}C NMR (δ, ppm): 112.7, 115.7, 134.8, 136.8, 136.1, 135.0 (aromatic); 115.9, C≡N free; 126.7, C≡N coord.

$[(NH_3)_5CoNC(CH_2)_2CNCo(NH_3)_5](ClO_4)_6\cdot H_2O$. Succinonitrile (0.40 g) and triflato complex (1.0 g) were dissolved in sulfolane and heated in a sealed flask at 70 °C for 3 h. The products were precipitated in ether, taken up in acidified water/acetone (5:1), and crystallized by adding 6 M $HClO_4$. The yellow complex was recrystallized from acidified water with concentrated $NaClO_4$, washed with ethanol and ether, and air-dried (0.30 g, 38%). IR (cm^{-1}): nitrile stretch 2300 (coord.) (*cf.* 2260 for free succinonitrile). Visible (0.05 M $HClO_4$, M^{-1} cm^{-1}): ϵ_{466} 126, ϵ_{332} 128. ^{1}H NMR (δ, ppm): 3.34, CH_2; 3.42, *trans* NH_3; 3.79, *cis* NH_3. ^{13}C NMR (δ, ppm): 14.9, CH_2; 129.5, C≡N.

Amido-*N*-Bonded Amide−Nitrile Complexes. These complexes were synthesized by base hydrolysis of the corresponding dinitrile complex.[2] The protonated forms were isolated by adding 6 M perchloric acid gradually to a cold concentrated solution of the amido-*N* complex. The bright yellow salts were filtered off, washed with ether only, and air-dried. They were stored in sealed vials in a freezer. Their NMR spectra were recorded in Me_2SO-d_6 with triflic acid added to inhibit deprotonation at the amide group.

$[Co(NH_3)_5$-(*E*)-$NHCOCH{=}CHCN](ClO_4)_2\cdot H_2O$. IR ($cm^{-1}$): nitrile stretch 2250. Visible (M^{-1} cm^{-1}, 0.1 M Tris): ϵ_{481} 76. ^{1}H NMR (δ, Me_2SO-d_6): 3.18, *trans* NH_3; 3.27, *cis* NH_3; 4.80, NH; 6.19, (d), CH^A; 7.09 (d),CH^B; J^{AB} = 16 Hz. ^{13}C NMR (δ, Me_2SO-d_6): 103.5, C^BH; 117.6, C≡N; 146.8, C^AH; 172.2, CONH.

$[Co(NH_3)_5$-(*E*)-$NHC(OH)CH{=}CHCN](ClO_4)_3\cdot H_2O$. IR ($cm^{-1}$): nitrile stretch 2260 cm^{-1}. Visible (M^{-1} cm^{-1}, 1.0 M HCl): ϵ_{478} 45. ^{1}H NMR (δ, Me_2SO-d_6): 3.20, *trans* NH_3; 3.26, *cis* NH_3; 6.19, (d), CH^A; 7.09, (d), CH^B (J^{AB} = 16 Hz); 7.21, NH.

$[Co(NH_3)_5NHCO(CH_2)_2CN](ClO_4)_2\cdot H_2O$. IR ($cm^{-1}$): nitrile stretch 2260. Visible (M^{-1} cm^{-1}, 0.1 M Tris): ϵ_{482} 65.0, ϵ_{348} 78.0. ^{1}H NMR (δ, Me_2SO-d_6): 2.54 (m), CH^{β}_2; 2.56 (m), CH^{α}_2; 3.13, *trans* NH_3; 3.21, *cis* NH_3; 3.86, NH. ^{13}C NMR (δ, Me_2SO-d_6): 13.6, $C^{\beta}H_2$; 34.2, $C^{\alpha}H_2$; 120.9, C≡N; 179.5, CONH.

$[Co(NH_3)_5NHC(OH)(CH_2)_2CN](NO_3)_2ClO_4\cdot H_2O$. This complex was crystallized by acidifying, as above a solution of the amide−nitrile complex which had been saturated with $NaNO_3$. IR (cm^{-1}): nitrile stretch 2250 cm^{-1}. Visible (M^{-1} cm^{-1}, 1.0 M HCl): ϵ_{475} 60.0, ϵ_{341} 61.5. ^{1}H NMR (δ, Me_2SO-d_6): 2.74 (m), CH^{α}_2; 2.81 (m), CH^{β}_2; 3.21, *trans* NH_3; 3.29, *cis* NH_3; 7.13, NH.

$[Co(NH_3)_5NHCO(CH_2)_3CN](ClO_4)_2\cdot H_2O$. IR ($cm^{-1}$): nitrile stretch 2260. Visible (M^{-1} cm^{-1}, 0.1 M Tris): ϵ_{483} 63.0, ϵ_{349} 75.5. ^{1}H NMR (δ, Me_2SO-d_6): 1.77 (m), CH^{β}_2; 2.30 (m), CH^{γ}_2; 2.50 (m), CH^{α}_2; 3.12, *trans* NH_3; 3.20, *cis* NH_3; 3.83, NH. ^{13}C NMR (δ, Me_2SO-d_6): 15.9, $C^{\gamma}H_2$; 22.2, $C^{\beta}H_2$; 38.5, $C^{\alpha}H_2$; 119.5, C≡N; 181.6, CONH.

$[Co(NH_3)_5NHC(OH)(CH_2)_3CN](ClO_4)_3\cdot H_2O$. IR ($cm^{-1}$): nitrile stretch 2260 cm^{-1}. Visible (M^{-1} cm^{-1}, 1.0 M HCl): ϵ_{474} 53.0, ϵ_{337} 51.5. ^{1}H NMR (δ, Me_2SO-d_6): 1.86 (m), CH^{β}_2; 2.48 (m), CH^{γ}_2; 2.56 (m), CH^{α}_2; 3.24, *trans* NH_3; 3.31, *cis* NH_3; 6.56, NH.

$[Co(NH_3)_5NHCO(CH_2)_4CN](ClO_4)_2\cdot H_2O$. IR ($cm^{-1}$): nitrile stretch 2250. Visible (M^{-1} cm^{-1}, 0.1 M Tris): ϵ_{485} 68.5, ϵ_{348} 84.0. ^{1}H NMR (δ, Me_2SO-d_6): 1.56 (4H, m), $CH^{\beta}_2CH^{\gamma}_2$; 2.19 (2H, m), CH^{ω}_2; 2.47 (2H, m), CH^{α}_2; 3.12, *trans* NH_3; 3.20, *cis* NH_3; 3.74, NH. ^{13}C NMR (δ, Me_2SO-d_6): 17.3, $C^{\omega}H_2$; 25.5, $C^{\gamma}H_2$; 26.4, $C^{\beta}H_2$, 40.3, $C^{\alpha}H_2$; 122.0, C≡N; 183.8, CONH.

(35) Mowry, D. T.; Butler, J. M. *Org. Synth.* **1950**, *30*, 46−48.
(36) Buckingham, D. A.; Cresswell, P. J.; Sargeson, A. M.; Jackson, W. G. *Inorg. Chem.* **1981**, *20*, 1647−1653.
(37) Jordan, R. B.; Sargeson, A. M.; Taube, H. *Inorg. Chem.* **1966**, 5, 1091−1094.

$[Co(NH_3)_5NHC(OH)(CH_2)_4CN](ClO_4)_3\cdot H_2O$. IR ($cm^{-1}$): nitrile stretch 2260. Visible ($M^{-1}\ cm^{-1}$, 1.0 M HCl): ϵ_{475} 61.0, ϵ_{341} 58.0. ^1H NMR (δ, Me_2SO-d_6): 1.62 (4H, m), $CH^{\beta}{}_2-CH^{\gamma}{}_2$; 2.51 (2H m), $CH^{\omega}{}_2$; 2.53 (2H, m), $CH^{\alpha}{}_2$; 3.26, *trans* NH_3; 3.34, *cis* NH_3; 6.97, NH.

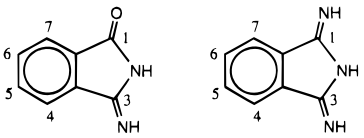
$(NH_3)_5CoNHCOC_6H_4$-2-CN$](ClO_4)_2\cdot H_2O$. The pentaammine(phthalonitrile) complex (0.65 g) was dissolved in ammonia buffer (15 mL, pH 10) and stirred for 1 min. The title complex was precipitated with solid $NaClO_4$ and recrystallized rapidly from aqueous Tris, washed with ethanol and ether and air-dried (0.25 g, 45%). IR (cm^{-1}): nitrile stretch 2240. Visible (0.1 M Tris, $M^{-1}\ cm^{-1}$); ϵ_{483} 77.5 (*cf.* ϵ_{484} 71). ^1H NMR (δ, Me_2SO-d_6): 7.59, 7.76, 7.83 (aromatic), *trans* NH_3; 3.35, *cis* NH_3; 4.74, NH. ^{13}C NMR (δ, Me_2SO-d_6): 142.4, 109.3, 132.8, 129.9, 134.0, 128.2 (aromatic); 118.6, C≡N; 175.3, CONH.

$[(NH_3)_5CoNHCOCH_2CN](ClO_4)_2\cdot H_2O$. $[(NH_3)_5CoNCCH_2CN](ClO_4)_3$ (2.00 g) was dissolved in acidified water (100 mL) and 1.0 M NaOH (30 mL) added. The solution was left to stir for 2 h, copious cobalt oxides were filtered off, and the complex was precipitated with solid $NaClO_4$ and a drop of 6 M $HClO_4$, and then filtered off. A second crop was obtained by acidifying the filtrate. The two crops were combined and recrystallized from aqueous Tris with concentrated $NaClO_4$ solution, washed with ethanol and ether, and air-dried (0.90 g, 53%). IR (cm^{-1}): nitrile stretch 2270. Visible ($M^{-1}\ cm^{-1}$, 0.10 M Tris): ϵ_{482} 78.0, $\epsilon_{340}{}^{sh}$ 130 (*cf.* ϵ_{480} 74, ϵ_{345} 95[2]). ^1H NMR (δ, Me_2SO-d_6): 3.58 (CH_2); 3.13, *trans* NH_3; 3.24, *cis* NH_3; 4.09, NH. ^{13}C NMR (δ, Me_2SO-d_6): 26.3 (CH_2); 117.2, C≡N; 171.0, CONH.

$[(NH_3)_5CoNHC(OH)CH_2CN](ClO_4)_3\cdot H_2O$. A concentrated solution of $[(NH_3)_5CoNHCOCH_2CN](ClO_4)_2$ was acidified gradually with 6 M $HClO_4$ to about pH 0. The solution remained orange in color. The title complex crystallized after the solution was chilled, and it was washed well with ether, air-dried, and stored in an air-tight container at 0 °C to inhibit deprotonation. It is not completely protonated as was shown by its orange-yellow color. IR (cm^{-1}): nitrile stretch 2270. Visible ($M^{-1}\ cm^{-1}$, 1.0 M HCl): ϵ_{477} 76.5, $\epsilon_{340}{}^{sh}$ 135. ^1H NMR (δ, Me_2SO-d_6): 3.58 (CH_2); 3.13, *trans* NH_3; 3.24, *cis* NH_3; 4.09, NH. ^{13}C NMR (δ, Me_2SO-d_6): 26.3 (CH_2); 117.2, C≡N; 171.0, CONH.

$[(NH_3)_5CoNHCO(CH_2)_2CONHCo(NH_3)_5](ClO_4)_4\cdot H_2O$. $[(NH_3)_5CoNC(CH_2)_2CNCo(NH_3)_5](ClO_4)_6$ (0.20 g) was dissolved in 0.1 M NaOH solution (10 mL) and left for 3 h. The solution was filtered to remove cobalt oxides, and the title complex was crystallized by adding $NaClO_4$. The orange complex was filtered off, washed with ethanol and ether, and air-dried (0.06 g, 36%). Visible (0.1 M Tris, $M^{-1}\ cm^{-1}$): ϵ_{481} 110, $\epsilon_{341}{}^{sh}$ 170. ^1H NMR (δ, ppm): 2.43, CH_2; 3.19, *cis* and *trans* NH_3; 3.73, NHCO. ^{13}C NMR (δ, ppm): 37.3, CH_2; 182.9, CONH.

$[Co(NH_3)_5NC(CH_2)_2CONH_2](ClO_4)_3\cdot H_2O$. A solution of $[Co(NH_3)_5NHCO(CH_2)_2CN](ClO_4)_2\cdot H_2O$ (0.70 g) in water (50 mL) was gradually acidified with 6 M $HClO_4$ until the orange solution turned yellow and was then left to stand for 1 h. The title complex crystallized after chilling and was recrystallized from acidified water with concentrated $NaClO_4$ solution, washed with ethanol and ether, and air-dried (0.56 g, 85%). IR (cm^{-1}): nitrile stretch 2320. Visible ($M^{-1}\ cm^{-1}$, 0.1 M $HClO_4$): ϵ_{467} 63.0, ϵ_{333} 57.0.^1H NMR (δ, Me_2SO-d_6): 2.52 (m), $CH^{\beta}{}_2$; 3.00 (m), $CH^{\alpha}{}_2$; 3.33, *trans* NH_3; 3.71, *cis* NH_3; 7.12, 7.57, $CONH_2$. ^{13}C NMR (δ, Me_2SO-d_6): 14.4, $C^{\alpha}H_2$; 28.9, $C^{\beta}H_2$; 133.0, C≡N; 171.1, $CONH_2$.



$[(NH_3)_5Co(2$-$NCC_6H_4CONH_2)](ClO_4)_3\cdot H_2O$. This complex was prepared by two methods: (1) $[(NH_3)_5CoNHCOC_6H_4$-2-CN$](ClO_4)_2\cdot H_2O$ was dissolved in water and the solution was gradually acidified with 6 M $HClO_4$ until it became bright yellow. The title complex was precipitated with excess acid and was filtered off, washed with ethanol and ether, and air-dried. Visible (0.1 M $HClO_4$, $M^{-1}\ cm^{-1}$) ϵ_{467} 83.5 (*cf.* ϵ_{467} 63[3]). IR (cm^{-1}): nitrile stretch 2280. ^1H NMR (δ, Me_2SO-d_6): 7.98, 8.12, 8.20 (aromatic); 3.44,*trans* NH_3; 3.86,*cis* NH_3; 8.18, 8.60, NH_2. ^{13}C NMR (δ, Me_2SO-d_6): 109.2, 137.9, 128.8, 136.4, 135.2, 132.4 (aromatic); 129.1, C≡N; 165.4, CONH.

(2) *2*-Cyanobenzamide (5.0 g) and the triflato complex (3.0 g) were dissolved in sulfolane which had been acidified with triflic acid. The solution was left stirring in a sealed flask for 3 h. (It is important not to heat the solution as this promotes isomerization to the 1-oxo-3-iminoisoindoline complex.) The yellow title complex was precipitated in ether and purified as for the phthalonitrile complex (0.51 g, 17%). The complex isomerizes in the solid state to form the 1-oxo-3-iminoisoindoline complex and therefore must be stored in the freezer.

$[(NH_3)_5CoNCCH_2CONH_2](ClO_4)_3\cdot H_2O$. Method 1. Cyanoacetamide (Fluka, 4.0 g) and the triflato complex (3.0 g) were heated in acetone (50 mL) and acidified with 1 drop of triflic acid at 60 °C for 1 h. Products were precipitated in ether and purified as for the pentaammine(malononitrile) species (1.6 g, 61%). IR (cm^{-1}): nitrile stretch 2320. visible ($M^{-1}\ cm^{-1}$, 0.10 M $HClO_4$): ϵ_{465} 63.5, ϵ_{332} 56.5 (*cf.* ϵ_{467} 63.3, ϵ_{333} 58.4[14]). ^1H NMR (δ, Me_2SO-d_6): 4.11 ($-CH_2-$); 3.35, *trans* NH_3; 3.79, *cis* NH_3; 7.63, 7.77, NH_2. ^{13}C NMR (δ, Me_2SO-d_6): 28.1 ($-CH_2-$); 128.6, C≡N; 168.7, $CONH_2$.

Method 2. An accurately known amount (∼0.25 g) of $[(NH_3)_5CoNHCOCH_2CN](ClO_4)_2$ was dissolved in water, which was then acidified with triflic acid, $[H^+] = 1$ M. The solution was left in a sealed flask for 17 h, diluted with water, and chromatographed on Sephadex. The resin was eluted first with 0.5 M $NaClO_4$ (pH 5), which separates first any unreacted amido-*N* complex (pH of the eluate was increased with solid Tris) and second a yellow 3+ complex; finally the pentaammineaqua complex was eluted with 0.75 M NaCl (pH 7). The yellow 3+ band was reduced in volume by rotary evaporation until crystallization occurred. The yellow solid was recrystallized from acidified water, and its ^1H and ^{13}C NMR spectra were recorded. The spectra were identical to those of the material obtained by method 1.

$[(NH_3)_5Co($1-oxo-3-aminoisoindolino-*endo*-*N*$)](ClO_4)_3\cdot H_2O$. The bright orange complex was prepared by acidifying a solution of $[(NH_3)_5Co$(1-oxo-3-iminoisoindolino-*endo*-*N*$)](ClO_4)_2$ with 6 M $HClO_4$. The product crystallized after chilling and was filtered off, washed with ether, and air-dried. Visible (1.0 M HCl, $M^{-1}\ cm^{-1}$): ϵ_{485} 68.0. ^1H NMR (δ, ppm): 3.31, *trans* NH_3; 3.63, *cis* NH_3; 7.83, (m), 8.10, (m), aromatic protons; 8.71, 10.53, $C-NH_2$. ^{13}C NMR (δ, ppm): 123.0, 123.3, C-4 and C-7; 132.8, 133.6, quaternary carbons; 134.4, 134.6, C-5 and C-6; 173.7, $C-NH_2$; 179.1, C═O.

Amidine-Bonded Complexes. The following amidine-bonded complexes were prepared by dissolving the appropriate dinitrile complex (0.50 g) in liquid ammonia (30 mL) at room temperature in an open beaker.[23] The solution was stirred to promote rapid evaporation of the excess ammonia, and the very soluble orange residue was recrystallized from concentrated $NaClO_4$ solution (average yield 50%).

$[Co(NH_3)_5NHC(NH_2)(CH_2)_2CN](ClO_4)_3\cdot H_2O$. IR ($cm^{-1}$): nitrile stretch 2260. Visible ($M^{-1}\ cm^{-1}$, H_2O): ϵ_{480} 74.5, ϵ_{340} 100. ^1H NMR (δ, Me_2SO-d_6): 2.60 (m), $CH^{\alpha}{}_2$; 2.82 (m), $CH^{\beta}{}_2$; 3.24, *trans* and *cis* NH_3; 5.67, $NHCNH_2$. ^{13}C NMR (δ, Me_2SO-d_6): 15.3, $C^{\beta}H_2$; 33.2, $C^{\alpha}H_2$; 19.5, C≡N; 172.1, $NHCNH_2$.

$[Co(NH_3)_5NHC(NH_2)(CH_2)_3CN](ClO_4)_3\cdot H_2O$. IR ($cm^{-1}$): nitrile stretch 2260. Visible ($M^{-1}\ cm^{-1}$, H_2O): ϵ_{483} 72.5, ϵ_{338} 110. ^1H NMR (δ, Me_2SO-d_6): 1.90 (m), $CH^{\beta}{}_2$; 2.40 (m), $CH^{\gamma}{}_2$; 2.56 (m), $CH^{\alpha}{}_2$; 3.23, *trans* and *cis* NH_3; 5.44, NHC_2. ^{13}C NMR (δ, Me_2SO-d_6): 16.8, $C^{\gamma}H_2$; 23.9, $C^{\beta}H_2$; 37.8, $C^{\alpha}H_2$; 120.6, C≡N; 174.8, $NHCNH_2$.

$[Co(NH_3)_5NHC(NH_2)(CH_2)_4CN](ClO_4)_3\cdot H_2O$. IR ($cm^{-1}$): nitrile stretch 2240. Visible ($M^{-1}\ cm^{-1}$, H_2O): ϵ_{481} 84.5, ϵ_{354} 100. ^1H NMR (δ, Me_2SO-d_6): 1.63 (4H, m), $CH^{\beta}{}_2CH^{\gamma}{}_2$; 2.31 (2H, m), $CH^{\omega}{}_2$; 2.51 (2H, m), $CH^{\alpha}{}_2$; 3.22, *trans* and *cis* NH_3; 5.36, $NHCNH_2$. ^{13}C NMR (δ, Me_2SO-d_6): 17.3, $C^{\omega}H_2$; 25.2, $C^{\gamma}H_2$; 27.3, $C^{\beta}H_2$, 38.3, $C^{\alpha}H_2$; 121.8, C≡N; 175.9, $NHCNH_2$.

$[Co(NH_3)_5($1,3-diiminoisoindolino-*endo*-*N*$)](ClO_4)_2\cdot H_2O$. $[Co(NH_3)_5NCC_6H_4$-2-CN$](ClO_4)_3$ (0.5 g) was dissolved in liquid ammonia (50 mL) in an open beaker. The excess ammonia was allowed to evaporate, and the dark pink residue was recrystallized from water with concentrated $NaClO_4$ solution. The complex was filtered off, washed with ethanol and ether, and air-dried (0.31 g, 72%). Visible ($M^{-1}\ cm^{-1}$, 0.1 M Tris): ϵ_{497} 68.0. ^1H NMR (δ, Me_2SO-d_6): 3.08, *trans* NH_3; 4.02, *cis* NH_3; 7.57, 7.93, (m), aromatic protons; 8.39, C═NH. ^{13}C NMR (δ, Me_2SO-d_6): 120.1, C_4 and C_7; 130.4, quaternary carbons; 133.9, C_5 and C_6; 172.9, C_1═NH, C_3═NH.

$[Co(NH_3)_5($1,3-diiminoisoindolino-*endo*-*N*$)](ClO_4)_3\cdot H_2O$. A concentrated solution of $[Co(NH_3)_5$(1,3-diiminoisoindolino-*endo*-*N*$)]$-

$(ClO_4)_2 \cdot H_2O$ was acidified with 6 M $HClO_4$, and a dark orange complex was crystallized, isolated by filtration, washed with ether, and air-dried. Visible (M^{-1} cm^{-1}, 1.0 M HCl): ϵ_{490} 65.5. ^1H NMR (δ, Me_2SO-d_6): 3.25, *trans* NH_3; 3.78, *cis* NH_3; 7.78, 8.13, 8.20, (m), aromatic protons; 7.90, C═NH; 9.75, 10.65, C−NH_2. ^{13}C NMR (δ, Me_2SO-d_6): 120.8, 122.4, C_4 and C_7; 132.0, 132.3, quaternary carbons; 133.0, 133.1, C_5 and C_6; 170.9, 171.9, C_1═NH, C_3−NH_2.

$[Co(NH_3)_5(2,5\text{-diiminopyrrolidino-}endo\text{-}N)](ClO_4)_2 \cdot H_2O$. $[Co(NH_3)_5NC(CH_2)_2CN](ClO_4)_3 \cdot H_2O$ (0.70 g) was added to liquid ammonia (50 mL) in an open conical flask which was placed in an ice/salt bath for 2 h, and extra liquid ammonia was added as required to keep the complexes in solution. The flask was then removed from the bath, and the excess ammonia was allowed to evaporate. The dark pink residue was crystallized from aqueous Tris with concentrated $NaClO_4$ solution, filtered off, washed with ethanol and ether, and air-dried (0.43 g, 73%). Visible (M^{-1} cm^{-1}, 0.1 M Tris): ϵ_{495} 64.0, $\epsilon_{361}{}^{sh}$ 121. ^1H NMR (δ, Me_2SO-d_6): 2.47, −CH_2−; 2.95, *trans* NH_3; 4.01, *cis* NH_3; 6.99, ═NH. ^{13}C NMR (δ, Me_2SO-d_6): 30.3, −CH_2−; 182.8, C═NH.

$[(NH_3)_5CoNH{=}C(CH_2)_2C(N){=}NHCo(NH_3)_5](ClO_4)_5 \cdot H_2O$. $[(NH_3)_5CoNC(CH_2)_2CNCo(NH_3)_5](ClO_4)_6$ (0.50 g) was dissolved in liquid ammonia in an open beaker and the solvent allowed to evaporate. The residue was crystallized from aqueous Tris by adding $NaClO_4$. The orange complex was filtered off, washed with ethanol and ether, and air-dried (0.11 g, 25%). Visible (0.1 M Tris, M^{-1} cm^{-1}): ϵ_{483} 190. ^1H NMR (δ, ppm): 2.82, CH_2; 3.23, *cis* and *trans* NH_3; 5.88, Co−NH═C. ^{13}C NMR (δ, ppm): 33.0, CH_2; 192.4, C═NH−Co.

Kinetic Data. The rates of base hydrolysis of the succinonitrile complex were monitored at 300−600 nm using a HP 8452A spectrophotometer. Equal volumes of a 0.020 M solution of $[Co(NH_3)_5NC(CH_2)_2CN](ClO_4)_3 \cdot H_2O$ and basic buffer (I = 2.00 M) were added to separate compartments of a bifurcated spectrophotometer cell. The solutions were rapidly mixed by inverting the cell, and the change in absorbance was measured. The buffers were solutions of ethanolamine partly neutralized with acetic acid, and sodium acetate was the supporting electrolyte. The pH of the buffers diluted to I = 1.00 M was determined potentiometrically: 0.010 HCl, I = 1.00 M (NaCl), was titrated with 1.0 M NaOH (ConVol).[25]

To determine whether the succinonitrile complex solvolyzed in aqueous acid or hydrolyzed to the amide-*N*-bonded species, a sample was dissolved in 1.0 M HCl and the absorbance changes were monitored at 90 min intervals for 24 h in the 500−450 nm range. The amide-*N* complex is reactive in aqueous acid, but no evidence for consecutive reactions was found. The rate of the amide-*N* to nitrile-bonded rearrangement for the succinic amide nitrile complex was monitored at 346 nm using a Cary 210 spectrophotometer. Equal volumes of a 0.020 M solution of $[Co(NH_3)_5NHCO(CH_2)_2CN](ClO_4)_2 \cdot H_2O$ and acid buffer (I = 2.00 M) were added to separate compartments of a bifurcated spectrophotometer cell. The solutions were rapidly mixed by inverting the cell, and the change in absorbance was measured. The buffers were solutions of glycine (0.050 M) partly neutralized with $HClO_4$, and $LiClO_4 \cdot 3H_2O$ was the supporting electrolyte. The pH of the buffers diluted to I = 1.00 M was determined potentiometrically: 0.010 HCl, I = 1.00 M ($LiClO_4 \cdot 3H_2O$), was titrated with 1.0 M NaOH (ConVol).[25]

The rates of solvolysis of the 1-oxo-3-iminoisoindoline and 1,3-diimino-isoindoline complexes were measured at 490 nm by dissolving samples of the complexes in 1 M CF_3SO_3H and 0.5 M HCl, respectively.

Reactions of Amide−Nitrile Complexes Bonded through the Amide Nitrogen. Samples (0.5 g) of all amide−nitrile complexes save the 2-cyanobenzamide complex were dissolved in 0.1 M NaOH (50 mL) and left in sealed flasks at room temperature for 3 days. The solutions were diluted with water and chromatographed on Sephadex. The columns were washed with water and eluted with 0.5 M $NaClO_4$. An orange band was obtained in each case, and the products were isolated by rotary evaporation of the solvent while the residue was stirred with ethanol and recrystallized from water. The products were identified by ^1H NMR spectroscopy.

Samples were dissolved in Me_2SO-d_6 that had been acidified with triflic acid. ^1H NMR spectra of the solution were recorded every 3 min for 1 h and then the same was done the next day for the 2-cyanobenzamide, fumaric amide−nitrile, 2-cyanoacetamide, and succinic amide−nitrile complexes. The ^{13}C NMR spectrum of each solution was measured at the end of the reaction. For the glutaric and adipic amide−nitrile complexes, ^1H NMR spectra were recorded at hourly intervals for 10 h and then after 24 h.

Samples (0.50 g) were dissolved in 1.0 M $HClO_4$ (50 mL) and the solutions left in sealed flasks for 24 h. The diluted solutions were chromatographed on Sephadex. The columns were washed with water and eluted with 0.5 M $NaClO_4$ (pH 5), an eluant which separates pentaammineaqua, amido-*N*, and nitrile-bonded complexes. The products were isolated as described above and were identified by nmr spectroscopy.

For the 2-cyanoacetamide complex, more than one product was obtained, and the distribution was determined as follows. An accurately known amount (∼0.25 g) was dissolved in water which was then acidified with CF_3SO_3H, $[H^+]$ = 1 M. The solution was left in a sealed flask for 17 h, diluted with water, and chromatographed on Sephadex. The resin was washed with water then eluted with 0.5 M $NaClO_4$ (pH 5), which separates first the unreacted starting material in the protonated form (as it left the column, this eluate was basified with Tris to prevent solvolysis); the nitrile-bonded species was eluted second. Finally, pentaammineaqua complex was removed from the column with 0.75 M NaCl (pH 7). The eluates were collected in volumetric flasks of suitable sizes and diluted to the mark. The absorbance of these solutions was measured (550−300 nm). The amount of each complex was determined from visible spectral data using 10 cm quartz cells ($[Co(NH_3)_5H_2O]^{3+}$ ϵ_{492} 50.5 M^{-1} cm^{-1},[36] $[Co(NH_3)_5NHCOCH_2CN]^{2+}$ ϵ_{482} 78.0 M^{-1} cm^{-1}, and $[Co(NH_3)_5NCCH_2CONH2]^{3+}$ ϵ_{465} 63.5 M^{-1} cm^{-1}).

Reactions of Amidine−Nitrile Complexes in Liquid Ammonia. Samples (0.20 g) of the amidine−nitrile complexes derived from (glutaronitrile)- and (adiponitrile)pentaamminecobalt(III) were dissolved in liquid ammonia (∼50 mL) in a conical flask which was placed in an ice/salt bath. After 2 h the solvent was allowed to evaporate, and the reaction products were chromatographed on Sephadex. The column was eluted with 0.5 M $NaClO_4$, and the products were isolated and identified as described above.

Acknowledgment. This work was supported by the Australian Research Council. We are grateful to the Microanalytical Service, Australian National University, for the microanalyses.

Supporting Information Available: Tables 2 and 3 of kinetic and spectrophotometric data (2 pages). Ordering information is given on any current masthead page.

IC960032G