of the dithiocarbamate ligand.

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Registry No. $(+)_{546}$-K[Co(EDTA)], 40029-01-4; $(+)_{546}$-K[Co((−)-PDTA))], 69176-58-5; $(+)_{546}$-Na[Co(EDDS)], 21670-22-4; $(+)_{546}$-Co(Me_2(dtc))$_3$, 69176-59-6; $(-)_{546}$-Co(Me_2(dtc))$_3$, 69176-60-9; $(+)_{546}$-Co(Et_2(dtc))$_3$, 69176-61-0; $(-)_{546}$-Co(Et_2(dtc))$_3$, 69176-62-1; $(-)_{546}$-Co(*i*-Pr_2(dtc))$_3$, 69176-63-2; $(+)_{546}$-Co(*i*-Pr_2(dtc))$_3$, 69176-64-3; $(+)_{546}$-Co(*n*-Bu_2(dtc))$_3$, 69176-65-4; $(-)_{546}$-Co(*i*-Bu_2(dtc))$_3$, 69176-66-5; $(+)_{546}$-Co(*i*-Bu_2(dtc))$_3$, 69176-67-6; $(+)_{546}$-Co(pyrr(dtc))$_3$, 69176-68-7; $(-)_{546}$-Co(pyrr(dtc))$_3$, 69176-69-8; $(+)_{546}$-Co(morph(dtc))$_3$, 69222-29-3; $(+)_{546}$-Co(Ph_2(dtc))$_3$, 52562-97-7; $(+)_{546}$-Co(Bz_2(dtc))$_3$, 69176-70-1; $(+)_{546}$-Co(*t*-Bu,CH_2CH_2OH(dtc))$_3$, 69120-61-2.

References and Notes

(1) Abbreviations used in this paper are as follows. R,R-dtc is N-substituted dithiocarbamate where R = Me (methyl), Et (ethyl), *i*-Pr (isopropyl), *n*-Bu (*n*-butyl), *i*-Bu (isobutyl), Bz (benzyl), or Ph, (phenyl), R,R = pyrr (pyrrolidyl) or morph (morpholyl), and R = *t*-Bu, CH_2CH_2OH (*tert*-butyl, 2-hydroxyethyl). EDTA = ethylenediaminetetraacetate anion; PDTA = 1,2-propanediaminetetraacetate anion; EDDS = ethylenediaminedisuccinate tetraanion; en = ethylenediamine (1,2-diaminoethane).
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Novel Reactions of 1,2-Disubstituted Benzenes Coordinated to Cobalt(III): Neighboring-Group Participation

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The pentaamminecobalt(III) complex of 1,2-dicyanobenzene reacts with a stoichiometric amount of base to give the coordinated carboxamido complex $(NH_3)_5$Co(2-carboxamidobenzonitrile)$^{2+}$. The latter complex cyclizes in base to the pentaamminecobalt(III) complex of 1-oxo-3-iminoisoindolin-2-yl. However, in acid solution the coordinated amide complex undergoes an intramolecular rearrangement to form the coordinated nitrile-free amide compound $(NH_3)_5$Co(2-cyanobenzamide)$^{3+}$. This nitrile complex is rapidly hydrolyzed, the reaction involving intramolecular catalysis by the free amide group. The product of the hydrolysis reaction, $(NH_3)_5$Co(2-carboxamidobenzamide)$^{2+}$, cyclizes in acidic solution to $(NH_3)_5$Co(1-oxo-3-iminoisoindoline)$^{3+}$ where the metal is coordinated to the exocyclic nitrogen (3 position). The characterization of the above complexes is described, and mechanisms for their formation are considered.

Introduction

The activating role of transition metals in promoting hydrolysis reactions is well-known.[1] For example, the hydrolysis of nitriles to carboxamides is accelerated by approximately 10^6–10^8 over that of the uncoordinated ligands.[2] Furthermore, rate enhancements are much larger for reactions where intramolecular paths are possible. Evidence for such paths involving coordinated nucleophiles has arisen mainly from kinetic data and the isolation of new complexes which can only result from the intramolecular reactions.[3]

In organic reactions intramolecular catalysis has been effected by the suitable positioning of functional groups (usually ortho to each other) on a single molecule. This mode of activation is termed neighboring-group participation.[4] One

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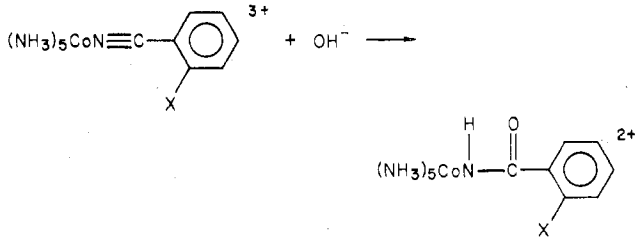
of the most important types of neighboring-group participation involves the neighboring group acting as a nucleophile, of which many examples are known.[5]

Relatively little is known, however, about the operation of neighboring-group effects in transition-metal complexes where presumably both the neighboring group and the transition metal contribute to activation. We have undertaken a study of neighboring-group effects in the hydrolysis of pentaamminecobalt(III)–nitrile complexes to carboxamido complexes where the nitrile is substituted at the 2 position.



It was anticipated that the hydrolytic products and/or rate enhancements would provide evidence for neighboring-group participation. In this paper we report on the unusual reactions of the pentaamminecobalt(III) complex of 1,2-dicyanobenzene and its derivatives and the characterization of the new complexes produced.

Experimental Section

Reagents. Nitrosyl tetrafluoroborate was purchased from Ventron Corp., Alfa Division, Danvers, Mass. Organic nitriles were obtained from the Aldrich Chemical Co. and were used without further purification. Rexyn 102(H) cation-exchange resin was obtained from Fisher Scientific, and CM-Sephadex C-25-120 was purchased from Sigma Chemical Co. Elemental analyses were performed by M-H-W Laboratories, Phoenix, Ariz.

Complexes. $[(NH_3)_5Co(1,2\text{-dicyanobenzene})](ClO_4)_3$, A. This complex was prepared as previously described.[6] Anal. Calcd for $[Co(NH_3)_5(NCC_6H_4CN)](ClO_4)_3$: C, 16.8; H, 3.33; N, 17.2. Found: C, 16.5; H, 3.80; N, 17.0.

$[(NH_3)_5Co(2\text{-carboxamidobenzonitrile})](ClO_4)_2$, B. This compound was prepared by slowly adding a stoichiometric amount of NaOH to a rapidly stirred solution of A. The original yellow solution, which is characteristic of the nitrile complexes, turns orange, indicating formation of the carboxamide. This solution was submitted to cation-exchange chromatography on CM-Sephadex. Two bands were obtained: a major orange band which moved down the column with the characteristics of a 2+ ion and a small amount of a pink band which remained at the top of the column. The 2+ band was eluted from the column with 0.5 M NaCl, the volume was reduced by half, and the complex was precipitated from solution by addition of $NaClO_4$. The pink band was not isolated. Anal. Calcd for $[Co(NH_3)_5(NHCOC_6H_4CN)](ClO_4)_2$: C, 19.7; H, 4.10; N, 20.1. Found: C, 19.6; H, 4.30; N, 19.5.

$[(NH_3)_5Co(1\text{-oxo-3-iminoisoindolin-2-yl})](ClO_4)_2$, C. Method I. Treatment of either A or B with excess base results in the formation of C which can be isolated by addition of solid $NaClO_4$. Anal. Calcd for $[Co(NH_3)_5(C_8H_5N_2O)](ClO_4)_2$: C, 19.7; H, 4.10; N, 20.1. Found: C, 19.1; H, 4.40; N, 19.5. This complex can also be isolated in the 3+ form, $[(NH_3)_5Co(1\text{-oxo-3-aminoisoindoline})](ClO_4)_3$, by addition of concentrated $HClO_4$. Anal. Calcd for $[Co(NH_3)_5(C_8H_6N_2O)](ClO_4)_3$: C, 16.3; H, 3.60; N, 16.7. Found: C, 16.1; H, 3.60; N, 16.5. The complex can also be precipitated as its hydrochloride by addition of concentrated HCl. Anal. Calcd for $[Co(NH_3)_5(C_8H_6N_2O)]Cl_3\cdot HCl$: C, 22.2; H, 5.10; N, 22.6. Found: C, 22.1; H, 5.80; N, 22.6.

Method II. The ligand 1-oxo-3-iminoisoindoline, $C_8H_6N_2O$ (mp 200 °C), was prepared via the cyclization of molten 2-cyanobenzamide (mp 172-173 °C).[7] The solid was recrystallized from acetonitrile. Nitrosyl tetrafluoroborate (0.8 g) was added to 20 mL of triethyl phosphate containing 4A molecular sieves, and the solution was allowed to stir for 15 min. To this solution 2 g of $[Co(NH_3)_5N_3](ClO_4)_2$ was added and the solution was stirred for a further 15 min. Finally, 2.5 g of 1-oxo-3-iminoisoindoline was added and the solution was heated on a steam bath for 1.5 h. The solution was added to a stirred mixture of 150 mL of 2-butanol and 150 mL of diethyl ether, and the resulting precipitate was filtered. The crude material was dissolved in water, filtered, and precipitated by addition of concentrated HCl. This was repeated twice. Anal. Calcd for $[Co(NH_3)_5(C_8H_6N_2O)]Cl_3\cdot HCl$: C, 22.2; H, 5.10; N, 22.6. Found: C, 22.2; H, 5.48; N, 22.3. This material was also converted to the perchlorate salt and recrystallized from dilute acid and dilute base. Analyses of both complexes gave identical results to those obtained in method I.

$[(NH_3)_5Co(2\text{-cyanobenzamide})](ClO_4)_3$, D. Treatment of a neutral solution of B (orange) with acid gives a quantitative conversion to D (yellow). The complex can be readily precipitated from solution as the perchlorate salt simply by using $HClO_4$ as the acid. Anal. Calcd for $[Co(NH_3)_5(NCC_6H_4CONH_2)](ClO_4)_3$: C, 16.3; H, 3.60; N, 16.7. Found: C, 16.1; H, 3.70; N, 16.4.

$[(NH_3)_5Co(2\text{-carboxamidobenzamide})](ClO_4)_2$, E. Addition of dilute base to the 2-cyanobenzamide complex, D, gives a quantitative yield of E. The complex can be obtained by addition of solid $NaClO_4$. Anal. Calcd for $[Co(NH_3)_5(NHCOC_6H_4CONH_2)](ClO_4)_2$: C, 19.0; H, 4.40; N, 19.4. Found: C, 19.3; H, 4.20; N, 19.3.

$[(NH_3)_5Co(1\text{-oxo-3-iminoisoindoline})]Cl_3\cdot HCl$, F. Addition of acid to a solution of E produces F. This complex precipitates readily as the hydrochloride when the acid is HCl. Anal. Calcd for $[Co(NH_3)_5(C_8H_6N_2O)]Cl_3\cdot HCl$: C, 22.2; H, 5.10; N, 22.6. Found: C, 22.6; H, 5.40; N, 23.1.

Kinetics. All rate measurements were carried out using a Durrum stopped-flow spectrometer or a Beckman Acta CIII spectrophotometer. For the base-hydrolysis reactions the nucleophile was kept in large excess over complex to ensure pseudo-first-order conditions. For the reaction B → D the acid concentration was in large excess over complex. Rate constants were evaluated from plots of log $(A_t - A_\infty)$ vs. time where A_t and A_∞ are the absorbances at time t and after the reaction was complete.

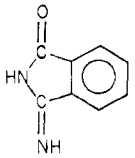
Physical Measurements. Electronic spectra were recorded with a Beckman Acta CIII spectrophotometer. The infrared spectra were obtained with a Beckman IR12. Proton magnetic resonance spectra were recorded with a Varian A-60A spectrometer. Mass spectra were obtained on a Varian MAT CH7 mass spectrometer.

Results

All of the complexes produced in this study were derived from the ligand 1,2-dicyanobenzene. The reactions of $(NH_3)_5Co(1,2\text{-dicyanobenzene})^{3+}$ and its derivatives are summarized in Scheme I.

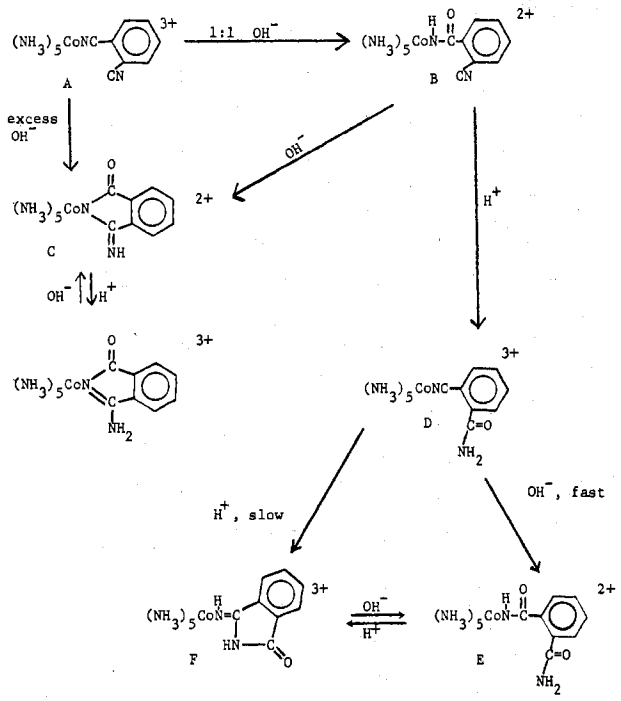
The 1,2-dicyanobenzene complex has been prepared previously[6] but the hydrolysis to the carboxamide was not studied. When A is treated with a stoichiometric amount of base, the expected carboxamido complex, B, is formed. B has been characterized by IR, NMR, and UV–visible methods. However, when A is treated with excess base, the product is the pentaamminecobalt(III) complex of 1-oxo-3-iminoisoindolin-2-yl, C. Surprisingly, when the amide-bonded complex B is dissolved in dilute acid (0.01 M), the nitrile-bonded 2-cyanobenzamide complex D is produced. This compound undergoes the expected hydrolysis to the diamide complex E. Furthermore, the diamide complex undergoes a facile rearrangement in acidic solution to form the pentaamminecobalt(III) complex of 1-oxo-3-iminoisoindoline, F, where the cobalt is coordinated to the nitrogen at the 3 position. This same complex can also be formed slowly by treatment of D with dilute acid.

Additional evidence for the cyclic nature of the ligand in complex C and its acid form is afforded by the direct preparation of the complex from the ligand 1-oxo-3-iminoisoindoline



Infrared Spectra. The infrared spectra of the complexes provide a good indicator of the various reactions outlined in

Scheme I



Scheme I. The parent compound $(NH_3)_5Co(1,2\text{-dicyanobenzene})^{3+}$, A, has bands at 2290 and 2240 cm^{-1} which can be attributed to the coordinated and free nitrile groups (for 1,2-dicyanobenzene, $\nu(C{\equiv}N)$ = 2235 cm^{-1}). The 1500–1700-cm^{-1} region of the spectrum is featureless, having only a broad band at 1620 cm^{-1} assigned to $\nu(NH_3)$ and two weak bands at 1595 and 1585 cm^{-1} due to $\nu(C{=}C)$ (aromatic). The carboxamido complex B has one band at 2225 cm^{-1} due to the uncoordinated nitrile group (for 2-cyanobenzamide, $\nu(C{\equiv}N)$ = 2228 cm^{-1}), and a band attributed to the carbonyl stretching frequency of the coordinated amide appears at 1585 cm^{-1}.

If either A or B is treated with excess base, a compound is produced which has no absorption bands in the 2000–2400-cm^{-1} region which can be associated with nitrile groups. Furthermore, two absorption bands are observed at 1680 and 1600 cm^{-1} which can be ascribed to $\nu(C{=}O)$ and $\nu(C{=}N)$, respectively. The free ligand 1-oxo-3-iminoisoindoline has $\nu(C{=}O)$ and $\nu(C{=}N)$ at 1724 and 1677 cm^{-1}. If this complex is precipitated from solution by adding concentrated HCl, the IR spectrum shows bands at 1740, 1682, 1625, and 1573 cm^{-1}. These data along with C, H, and N analyses, an alternate preparation (see Experimental Section), and other physical evidence have led us to formulate the complex as C in Scheme I.

Perhaps the most surprising result is obtained when the 2-carboxamidobenzonitrile complex is treated with dilute acid. The solution changes from orange to yellow and the product is easily precipitated from solution with $NaClO_4$. The IR spectra of both B and the complex D, produced by treating B with acid, are shown in Figure 1 over the range 1500–2400 cm^{-1}. The appearance in the spectrum of D of a strong band at 2295 cm^{-1} indicates a coordinated nitrile group whereas in the spectrum of B the peak is at 2225 cm^{-1} and characteristic of a free nitrile group. In D the carbonyl stretching frequency is observed at 1680 cm^{-1} very near that for $\nu(C{=}O)$ of 2-cyanobenzamide. Thus D has been formulated as the nitrile-bonded complex of 2-cyanobenzamide.

Addition of base to the 2-cyanobenzamide complex D produces the expected diamide complex. E has three bands in the carbonyl region at 1667, 1610, and 1587 cm^{-1}. These bands can be assigned to the C=O stretching frequency of the free amide, the C–N stretch in the coordinated amide, and the C=O stretch in the coordinated amide, respectively.

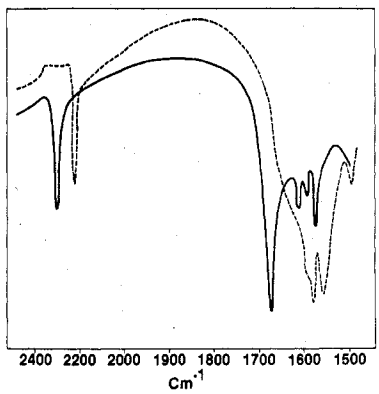
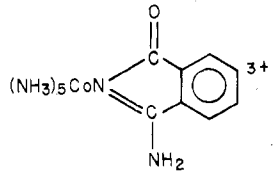


Figure 1. Infrared spectra of $(NH_3)_5Co(2\text{-carboxamidobenzonitrile})^{2+}$, B, ---, and $(NH_3)_5Co(2\text{-cyanobenzamide})^{3+}$, D, —.

Finally, F is produced from E "instantaneously" by addition of acid or over a period of 24 h from an acid solution of D. Complex F has no nitrile bands. Bands at 1760 and 1670 cm^{-1} can be assigned to $\nu(C{=}O)$ and $\nu(C{=}N)$ stretches by comparison to the infrared spectrum of the free ligand, 1-oxo-3-iminoisoindoline.

Electronic Spectra. The wavelength of the band of $^1A_{1g} \rightarrow {}^1T_{1g}$ parentage for the two nitrile-bonded complexes A (466 nm (66 M^{-1} cm^{-1}) and D (467 nm (63 M^{-1} cm^{-1})) lies at a lower value than that observed for $Co(NH_3)_6^{3+}$, as expected. Upon addition of base to A and D the peak maxima shift irreversibly to lower energy, consistent with production of the carboxamido derivatives B (484 nm (71 M^{-1} cm^{-1})) and E (479 nm (71 M^{-1} cm^{-1})), respectively. Furthermore, a spectrum identical with that of D is obtained when acid is added to a solution of the 2-carboxamidobenzonitrile complex B.

The spectrum of the 1-oxo-3-iminoisoindolin-2-yl complex changes only slightly in the visible region when recorded in 1.0 M $HClO_4$ (from 490 nm (63 M^{-1} cm^{-1}) to 488 nm (64 M^{-1} cm^{-1})). However, in the ultraviolet region the 1-oxo-3-iminoisoindolin-2-yl complex has maxima at 302 and 296 nm in H_2O whereas in 1.0 M $HClO_4$ the maxima appear at 298, 279, and 272 nm. Presumably this is due to protonation of the ligand and so we propose the structure



Although there are two other sites available for protonation, the exocyclic nitrogen is favored because of the NMR results.

Proton Magnetic Resonance Spectra. The chemical shifts of the various protons of the complexes are listed in Table I. These tend to confirm the assignments in Scheme I. The spectra of the nitrile- and carboxamido-coordinated complexes are typical of those observed previously.[6]

The spectrum of the $(NH_3)_5Co(1\text{-oxo-3-iminoisoindolin-2-yl})^{2+}$ complex is shown in Figure 2 along with the spectrum of the ligand 1-oxo-3-iminoisoindoline. In the complex, the resonance at 9.30 ppm has been attributed to the C=NH proton. Upon acidification this peak disappears, presumably because of broadening due to rapid exchange. This tends to support the 1-oxo-3-aminoisoindoline structure given previously (see Electronic Spectra). The broad multiplet centered at 8.00 ppm integrates for one proton and is assigned to aromatic proton H_a whereas the peaks centered at 7.61 ppm are comprised of H_b, H_c, and H_d. This assignment was made on the basis of spin-decoupling experiments. Saturation of the

Table I. Proton Magnetic Resonance Spectra of Complexes in Scheme I[a]

complex	chemical shift, ppm		
	cis NH_3	trans NH_3	others
A	3.82	3.44	C_6H_4 8.10[b]
B	3.35	3.23	NH 4.71
			C_6H_4 7.74[b]
C	3.72	3.20	C_6H_4 7.61, 8.00
			C=NH 9.30
D	3.81	3.42	C_6H_4 7.95[b]
			NH_2 8.67
E	3.58	3.38	C_6H_4 7.65[b]
			NH_2 6.67
F	3.68	3.52	C_6H_4 7.84, 8.30
			NH 8.90

[a] Solvent is Me_2SO-d_6. All chemical shifts are relative to the solvent peak at 2.52 ppm. [b] Center of multiplet.

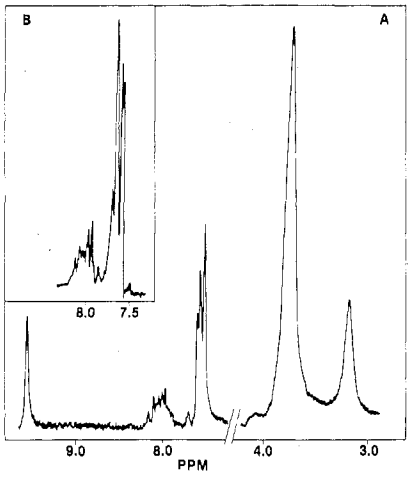
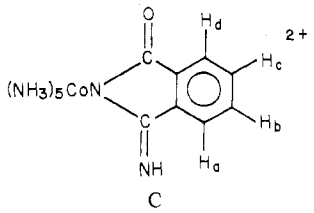


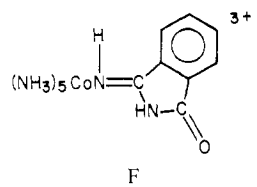
Figure 2. Proton magnetic resonance spectra of (A) $(NH_3)_5Co(1\text{-oxo-3-iminoisoindolin-2-yl})^{2+}$ and (B) 1-oxo-3-iminoisoindoline in Me_2SO-d_6.

resonance at 8.00 ppm results in the collapse of all fine structure at 7.61 ppm leaving a single peak.



C

The NMR spectrum of F is similar to that described for C and the structure below is proposed where the cobalt is now



F

coordinated to the exocyclic nitrogen. The resonance at 8.90 ppm is probably due to the proton on the endocyclic nitrogen. The remaining proton on the coordinated nitrogen could not be located and may be hidden under the broad resonance at 3.68 ppm.

The chemical shift difference between the cis and trans NH_3 resonances indicates that all of the complexes A–F are nitrogen bonded.[8]

Kinetics. The kinetic data support the reactions outlined in Scheme I. Table II contains some of the preliminary data obtained. The data obtained for reaction A → B are typical of that obtained for the hydrolysis of other $(NH_3)_5CoNCR^{3+}$ complexes. The corresponding hydrolysis reaction D → E indicates enhanced reactivity due to the 2-amido substituent. The reaction B → D was quite unexpected, and the first-order rate constant given was extracted for the mechanism given in the Discussion.

Table II. Kinetic Data for Reactions Outlined in Scheme I[a]

reaction	conditions	rate constant
A → B	$[OH^-]$ = 0.00800–0.0500	1050 M^{-1} s^{-1} [b]
B → C	$[OH^-]$ = 0.0100–0.300	1.1 M^{-1} s^{-1} [b]
B → D	$[H^+]$ = 0.100–1.00	0.31 s^{-1} [c]
D → E	$[OH^-]$ = (6.00–182) × 10^{-7}	5.8 × 10^6 M^{-1} s^{-1} [d]

[a] t = 25 °C, I = 1.0 M ($LiClO_4$). [b] Rate constant obtained by dividing k_{obsd} by $[OH^-]$. [c] Rate constant extracted from a plot of k_{obsd}^{-1} vs. $[H^+]^{-1}$. [d] Tris buffer.

Discussion

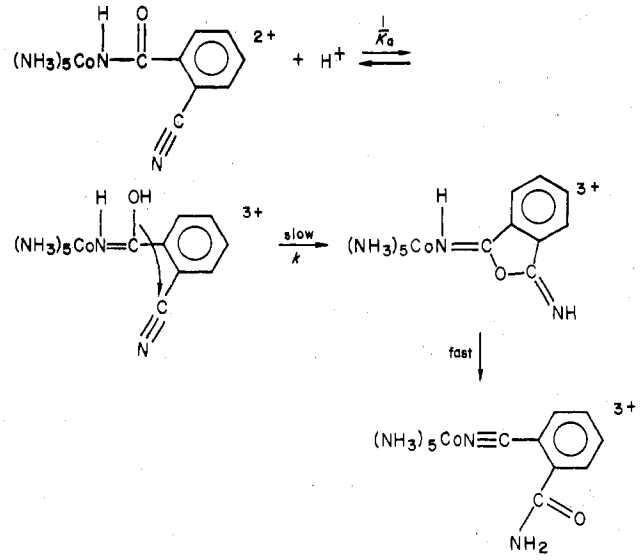
The formation of the 1-oxo-3-iminoisoindolin-2-yl complex, C, from the 2-carboxamidobenzonitrile complex, B, and base is not unexpected. Uncoordinated 2-cyanobenzamide also reacts with OH^- to form 1-oxo-3-iminoisoindoline.[7,9] C is also formed from the 1,2-dicyanobenzene complex. Kinetic data show that B is formed 1000 times faster than its cyclization to C, and the sequence below is indicated. Apparently the metal has very little influence on the cyclization reaction since the rate constants for coordinated and uncoordinated reactions are approximately the same.[10]

$$A \xrightarrow[OH^-]{1050\ M^{-1}\ s^{-1}} B \xrightarrow[OH^-]{1.1\ M^{-1}\ s^{-1}} C$$

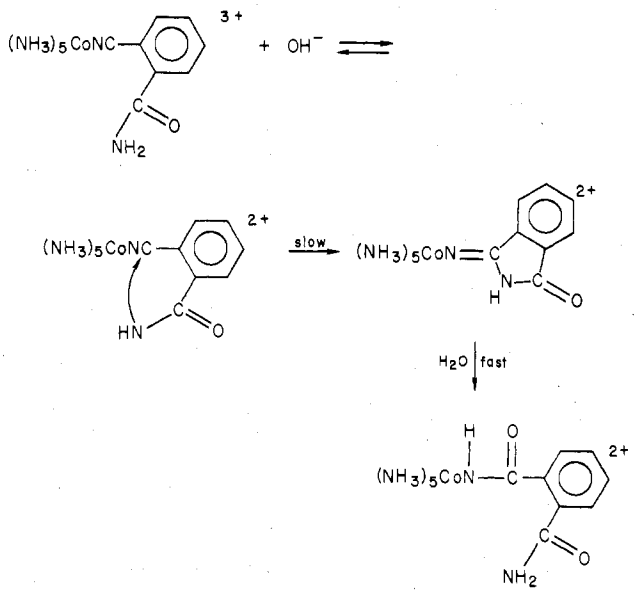
The most unusual reaction is observed between complex B and hydrogen ion. B rearranges in acidic solution to the nitrile-bonded 2-cyanobenzamide complex D. Generally, cobalt(III) substitution reactions occur by dissociative processes, and rearrangement via a seven-coordinate intermediate does not seem likely. However, when the conversion is carried out in the presence of chloride or azide ions, no $(NH_3)_5CoCl^{2+}$ or $(NH_3)_5CoN_3^{2+}$ is detected. Furthermore, no aquopentaamminecobalt(III) is detected during cation-exchange chromatography. These competition experiments rule out the dissociative path most generally employed by cobalt(III). The fact that the reaction is complete in a few seconds at room temperature also mitigates against a dissociative process since ligand exchange on cobalt(III) is extremely slow. One method of conversion consistent with the previous observations is an intramolecular rearrangement via an isoimide intermediate as shown in Scheme II. Protonation at oxygen in a carboxamide complex has been observed previously,[2a] and this could provide the driving force for formation of the cyclic intermediate. Preliminary kinetic data for this reaction are consistent with this interpretation giving pK_a = 0.4 and k = 0.31 s^{-1} at 25 °C and I = 1.0 M ($LiClO_4$). The rather small value of the pK_a is consistent with that observed for other coordinated amides.[6]

The base hydrolysis of the nitrile-bonded 2-cyanobenzamide produces the expected diamide product E. However, the reaction is unusually rapid having a rate constant of approximately 10^6 M^{-1} s^{-1} at 25 °C and I = 1.0 M ($LiClO_4$). This is a factor of a 1000 times larger than that observed for similar hydrolyses with other ortho groups and cannot be rationalized on the basis of ring substituent effects alone. Since amides are known to catalyze a wide variety of hydrolytic processes via intramolecular nucleophilic attack,[4,5,11] the further rate enhancement in the above process may be attributed to a neighboring-group effect by the uncoordinated amide. Both the nitrogen and oxygen atoms of the amide group can act as nucleophiles, but in basic solution N attack is favored.[4b] A

Scheme II



Scheme III

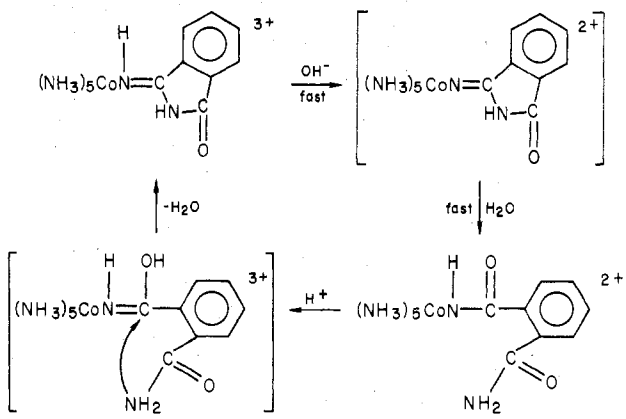


possible mechanism for this reaction is given in Scheme III.[12]

The diamide product produced in Scheme III undergoes an interesting rearrangement in acidic solution to form what we believe is a complex of 1-oxo-3-iminoisoindoline coordinated through the exocyclic (3-N) nitrogen (See F in Scheme I). The proposed structure is based on C, H, and N analyses, NMR, IR, and UV–visible spectra, and mass spectral data. The mass spectra of the acid form of complex C and of complex F both yield peaks at m/z 146 at 200 °C while at 300 °C the parent peak is at m/z 147. This indicates a change from 1-oxo-3-iminoisoindoline to phthalimide. Furthermore, isolation of the free ligand from the complex by reduction of Co(III) to Co(II) indicates 1-oxo-3-iminoisoindoline as a constituent in the acidic form of both C and F. The reaction E → F is reversible and the original diamide is produced at alkaline pH. Attempts to study this reaction failed because the reaction was complete within the deadtime of the stopped-flow. A mechanism consistent with these observations is given in Scheme IV.[13]

The reactions described in Scheme I are of interest both from a synthetic point of view in building up novel heterocyclics

Scheme IV



and from a kinetic point of view with respect to neighboring-group interactions. The latter effect appears to provide a novel complementary activation along with the metal to give hydrolysis rates approaching enzymatic processes.

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Registry No. A, 53739-01-8; B, 69120-37-2; C, 69120-39-4; D, 69120-41-8; E, 69120-43-0; F, 69120-44-1; $[(NH_3)_5Co(1\text{-oxo-}3\text{-aminoisoindoline})](ClO_4)_3$, 69155-27-7; $[(NH_3)_5Co(1\text{-oxo-}3\text{-aminoisoindoline})]Cl_3 \cdot HCl$, 69120-45-2; 1-oxo-3-iminoisoindoline, 14352-51-3; $[Co(NH_3)_5N_3](ClO_4)_2$, 14283-04-6.

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(12) Participation of the amide oxygen as the intramolecular nucleophile is also possible.

(13) Amide planarity may not favor intramolecular attack by NH_2 in acidic media. An alternate possibility involves attack by –OH on the free amide carbon. This would then result in F having an isoimide structure and an isoimide intermediate in Scheme IV.