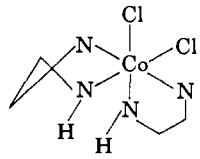

Figure 8. Schematic diagram showing the two least sterically hindered NH protons (designated as H_c in text) in the *cis*-dichlorobis(ethylenediamine)cobalt(III) ion. All other NH protons are adjacent to either one or two chlorine atoms.

possibility that they arise from protons in different molecules.

For *trans*-$[Co(en)_2Cl_2]Cl$, the steric hindrance due to the large size of the chlorine atoms would prevent the formation of a stable secondary coordination shell. The two stable conformations of each ethylenediamine ring may then be in rapid equilibrium. Therefore, we can no longer differentiate between axial and equatorial hydrogens. As a result, there is only one broadened NH signal in both DMSO-d_6 and D_2O–D_2SO_4. The appearance of an overlapped five-line signal for the CH proton in D_2O further confirms the rapid equilibrium between the conformers of the ethylenediamine ring. A small difference (0.18 ppm) for δ_{NH-CH} in the two kinds of solvents suggests the existence of a very weak second coordination shell for the *trans* complex in DMSO-d_6.

In each of the ethylenediamine rings in *cis*-$[Co(en)_2Cl_2]Cl$ there are two NH hydrogens (designated by H_a) *cis* to two Cl atoms and two NH_2 groups, and two NH hydrogens *cis* to one Cl atom and three NH_2 groups. Of the latter two NH hydrogens, one is adjacent to one Cl and one NH_2 group (designated as H_b); the other is adjacent to two NH_2 groups (designated as H_c) (Figure 8). As in the case of the *trans* complex, the two H_a hydrogens and the H_b hydrogen would not form stable second coordination bonds because of steric hindrance. However, H_c is capable of forming a definite hydrogen bond with a solvent molecule. In D_2O at 35°, the hydrogen bonding is probably not very strong so that H_b and H_c appeared as unresolved absorptions (−1.50 ppm from the center of the CH absorption); the H_a protons absorbed at a lower field (−2.77 ppm) because of the influence of two *cis* Cl atoms.[5] When the temperature was lowered, the H_c absorption appeared as a separate peak because of the formation of more definitive hydrogen bonding (Figure 4d). The CH protons showed some fine structure, but were not well resolved. (Three peaks of 1:1:2 ratio for the NH protons in *cis*-$[Co(en)_2(NH_3)_2](ClO_4)_3$ were also observed in acidified D_2O with the H_a peak at a higher field than the H_b and H_c peaks.[9]) In DMSO-d_6, the solvent molecule can form a stronger hydrogen bond with the H_c hydrogens in *cis*-$[Co(en)_2Cl_2]Cl$. As a result, the H_c signal moved further downfield; in the case we studied, this signal superimposed on the H_a signal. Therefore, the intensity of the two peaks at δ_{NH-CH} −1.26 and −2.85 ppm have the ratio 1:3. The difference in the chemical shift for the H_c proton in D_2O (with 0.0175 mole fraction of D_2SO_4) and in DMSO-d_6 is 0.94 ppm, which is the same as that for the NH protons of $[Co(en)_3]^{3+}$ in the two solvents. This may serve as another evidence for the existence of secondary coordination due to hydrogen bonding between the ligands in a complex and the solvent molecules.

Acknowledgment. The author wishes to thank Drs. T. E. Haas and R. D. Stolow for helpful discussions. The support from the Tufts University Research Fund is also acknowledged.

Electron Transfer through Organic Structural Units. IV. N-Coordinated Pyridines as Bridging Groups in Oxidation–Reduction Reactions[1]

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Contribution from the Department of Chemistry, San Francisco State College, San Francisco, California. *Received May 22, 1967*

Abstract: The specific rates of reduction of six substituted pyridinepentaamminecobalt(III) complexes, and the pyrazolepentaamminecobalt(III) complex, with Cr^{2+} have been measured. In these complexes, acetyl- and benzoylpyridines coordinate through the ring nitrogen, as does N,N-dimethylnicotinamide; 2- and 4-hydroxypyridine coordinate through oxygen. Rate constants for the unsubstituted pyridine and pyrazole complexes, and for the 2-OH-, 4-OH-, and 3-$(CH_3)_2NCO$-substituted pyridine derivatives, lie in the range 0.002–0.03 l. mole^{-1} sec^{-1} (24.5°, μ = 1.2), whereas the acetyl and benzoyl derivatives have values in the range 10^2–10^4 l. mole^{-1} sec^{-1}. The 4-benzoylpyridine complex is reduced more rapidly than any other organic pentaamminecobalt(III) derivative thus far reported, except for a few which form chelated Cr(III) products. These rates are not acid dependent. The ketopyridine complexes, like the unsubstituted pyridine complex, give $Cr(H_2O)_6^{3+}$ as the sole isolable Cr(III) product, but the very striking accelerations (five to six powers of ten) resulting from incorporation of the carbonyl substituent strongly indicate direct participation of the carbonyl group in the electron-transfer process, *i.e.*, reduction by remote attack. Surprisingly, rate increases for 3-keto substitution in Co(III)-bound pyridine are nearly as great as for 4-keto substitution.

The reduction, with Cr(II), of pentaamminecobalt(III) complexes may be substantially accelerated by introducing an appropriately substituted pyridine as a sixth ligand at the Co(III) center. Earlier papers in this

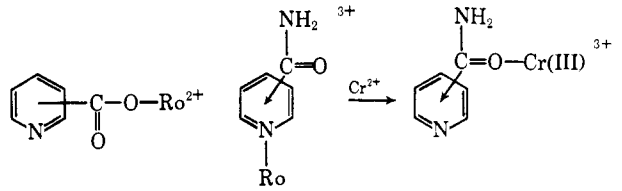
(1) This research was sponsored by the Faculty Development Fund at San Francisco State College. This support is gratefully acknowledged.

Table I. Pentaamminecobalt(III) Perchlorates, $RCo(NH_3)_5(ClO_4)_3$

R	Heating time, min (°C)	% Co Calcd	% Co Found[a]	λ_{max}, mμ	ϵ_1	λ_{max}, mμ	ϵ_2	$\nu_{C=O}$,[b] cm^{-1}
N-Coordinated ligands								
Pyridine	20 (70)	11.4	11.4	475	64.0	348[c]	67.5	
3-Acetylpyridine (IV)	35 (75)	10.2	9.9	474	64.5			1710
3-Benzoylpyridine (V)	60 (100)	9.2	9.3	476	76.5			1665
N,N-Dimethylnicotinamide (VI)	60 (100)	9.8	10.0	475	63.2	334	86.5	1632
4-Benzoylpyridine (VII)	55 (100)	9.2	9.3	474	66.5			1675
Pyrazole (X)	20 (100)	11.6	11.6	481	98.0			
O-Coordinated ligands								
N,N-Dimethylformamide		11.4	11.4	523	105	347	62.5	1660
4-Hydroxypyridine (VIII)	10 (100)	11.0	11.1	519	107	360[d]	96	1640[e]
2-Hydroxypyridine (IX)	10 (100)	11.0	11.0	510	68.0	360[d]	132	1645[e]

[a] See ref 2a. [b] KBr pellet. [c] Maxima in addition to those listed are at 265 mμ (ε 3000), 258 (4300), and 253 (4700). [d] Shoulder. [e] See ref 8.

series reported that pyridinecarboxylato complexes (I) having a cobalt(III)-bound carboxyl α or γ (but not β) to the ring nitrogen were reduced 10^3–10^6 times as rapidly as the corresponding benzene derivatives, leading to the suggestion that electron transfer was occurring through the pyridine nitrogen.[2] More recently, Nordmeyer and Taube[3] have described the Cr(II) reductions of ring-

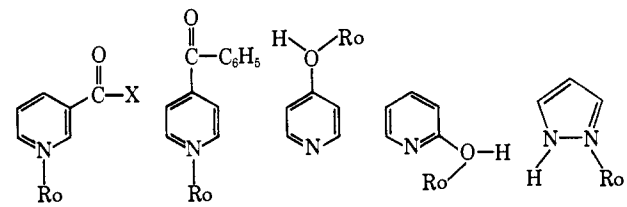


I(2-,4-) II(3-,4-) III

Ro = "roseo" = $Co(NH_3)_5$

coordinated pyridinecarboxamide derivatives (II) yielding chromium complexes (III) in which chromium appears to be bound to the carboxamide group, remote from the Co(III)-bound site in the reactant. The latter study provided a very direct experimental backing for the notion of reduction by remote attack which was forwarded over a decade ago[4] to account for rapid reduction of Co(III) complexes of α,β-unsaturated dicarboxylic acids, systems in which the symmetry of the ligands precluded direct chemical support of the proposed mechanism.

The present report deals with the preparation and reduction of additional $Co(NH_3)_5$ derivatives of substituted pyridines (IV–IX) and the corresponding complex of pyrazole (X). Of principal interest here is the introduction of keto groups into a bound pyridine ligand, for



IV, X = CH_3 VII VIII IX X
V, X = C_6H_5
VI, X = $N(CH_3)_2$

there is evidence that such groups support reduction *via* remote attack in the benzene series.[2] As is the case for benzoato complexes, such carbonyl substitution has been found to accelerate reduction, but here the effects are much more dramatic.

Experimental Section

Materials. Aquopentaamminecobalt(III) perchlorate, chloropentaamminecobalt(III) perchlorate, sodium and lithium perchlorate solutions (for kinetic experiments), and chromous solutions were prepared as described.[2a] Concentrations of Cr(II) solutions were determined from the absorbances of the parent $Cr(ClO_4)_3$ solutions; 1 *M* Cr(II) solutions were used within a week after their preparation, whereas more dilute solutions (0.25 *M* or less) were used within 2–3 days. (It was shown independently that reduction of $Cr(ClO_4)_3$ solutions to Cr(II) under these conditions resulted in a volume increase of less than 2%.) Heterocyclic ligands (Aldrich and Eastman products) were used as received.

Cation-exchange resin (Bio-Rad 50W-X2, 200–400 mesh), used in separating reaction products, was pretreated successively with distilled water, 6 *N* NaOH, water, 15% H_2O_2, water, 20% $HClO_4$, water, 50% acetone, and water. The resulting product was then eluted with 0.02 *M* $HClO_4$ until materials absorbing in the range 375–400 mμ were absent from the eluate.

Preparation of the Complexes. The complexes were prepared by treatment of aquopentaamminecobalt(III) perchlorate or N,N-dimethylformamidopentaamminecobalt(III) perchlorate[2b] with a fivefold excess of the ligand. Heating times and temperatures are listed in Table I. The 2-hydroxypyridine derivative was prepared from the aquo perchlorate, and the pyrazole derivative from the DMF complex, merely by heating with the free heterocycle in the absence of solvent; for the 4-hydroxypyridine derivative, the ligand was dissolved in a minimum volume of diethylene glycol diethyl ether at 95° before addition of the aquo perchlorate. At the conclusion of the heating period in these three cases, the reaction mixture was dissolved in an equal volume of warm water, the solution quickly cooled to 5°, and saturated aqueous $NaClO_4$ added until precipitation occurred. The complexes, as their perchlorates, were then filtered off and recrystallized from 1 *N* perchloric acid.

The preparation of complexes of the less polar benzoylpyridine derivatives was more troublesome. Typically, 3 g of the aquo perchlorate was converted to the DMF complex by treatment with 4 ml of dimethylformamide at 95°; to the resulting slurry was added 4.5 g of the heterocyclic ligand and the mixture was heated while stirring was maintained. As conversion proceeded, the rose color in solution changed to a deep orange, but prolonged heating until development of a yellow-brown color should be avoided, for the desired complexes undergo slow decomposition at the reaction temperatures.[5] At the conclusion of the heating period, the mixture was extracted with two 150-ml portions of ether and the ether extracts were discarded. To the pasty material remaining was added 100 ml of warm methanol. The mixture was cooled and filtered to remove the unreacted DMF complex and the $Co(NH_3)_6(ClO_4)_3$ formed by decomposition. The filtrate was concentrated to 30 ml by rotary evaporation, and 10 ml of a saturated

(2) (a) E. S. Gould and H. Taube, *J. Am. Chem. Soc.*, **86**, 1318 (1964); (b) E. S. Gould, *ibid.*, **87**, 4730 (1965).
(3) F. R. Nordmeyer and H. Taube, *ibid.*, **88**, 4295 (1966).
(4) H. Taube, *ibid.*, 77, 4481 (1955).

(5) Two modes of decomposition were observed when these complexes were overheated. The first appears to involve oxidation of the ligand and reduction of cobalt to Co(II); in the second, the complex undergoes ligand redistribution (in a manner not yet clear) to yield, as the principal isolable product, $Co(NH_3)_6(ClO_4)_3$. The first of these decomposition paths predominates with the keto-substituted pyridines.

methanolic solution of NaI added, slowly precipitating the desired complex as its iodide.[6] The yellow iodide was filtered off and washed with ethanol, then with ether, and was recrystallized immediately from a minimum volume of water at 70°. The recrystallized iodide was redissolved in water, and, after careful acidification with 1 *M* $HClO_4$, an equal volume of saturated $NaClO_4$ was added. The solution was cooled to 10° and rapidly filtered, and the filtrate (which should be yellow) cooled slowly at −10°. The precipitated complex perchlorate was then filtered off and dried in air. With the 3-acetylpyridine derivative, the treatment with methanol was omitted, and the residue from the ether extraction was dissolved directly in 7 ml of water and filtered; the complex iodide was precipitated from aqueous solution by addition of saturated aqueous NaI. With the N,N-dimethylnicotinamide derivative, no dimethylformamide was used; instead, the aquo complex was added to the molten ligand and 2 ml of diglyme was added. At the conclusion of the reaction, the mixture was diluted with water and filtered, and the complex iodide was precipitated and converted to the perchlorate in the usual way.

None of these procedures was effective in preparing pyridinepentaamminecobalt(III) complexes having the following ring substituents: 2-, 3-, and 4-amino; 3- and 4-aldehydo; 3-hydroxy; 2-cyano; 3-carbethoxy; 3-bromo; 2-acetamido; and 4-acetyl. Similarly, these methods failed when applied to the preparation of $Co(NH_3)_5$ complexes of quinoline, pyrazine, and benzotriazole. The reactions with 3- and 4-cyanopyridine yielded products which appeared to be cyanopyridine derivatives. but these could not be satisfactorily purified. In reactions with 2-acetyl- and 2-benzoylpyridine, the principal isolable products (even after only a few minutes of heating) were bright yellow solids which, unlike the other pyridine complexes in this series, were sparingly soluble in water and in ethanol and which exhibited an absorption maximum at 443 mμ, rather than at the expected 474–480 mμ. Basic hydrolysis of these substances to Co_2O_3 could be accomplished only by prolonged heating with concentrated alkali, in contrast to the usual pentaamminecobalt(III) complexes which are destroyed by a few minutes' heating with 0.1 *N* NaOH.[7]

Spectra of the Complexes. Visible absorption maxima for the complexes prepared are listed in Table I, together with extinction coefficients. The acetyl-, benzoyl-, and dimethylcarboxamido-substituted pyridine complexes exhibit a maximum at 474–476 mμ with an ϵ_{max} value of 63–77, very close to the corresponding values for the unsubstituted pyridine[2b] and pyridinecarboxamide[3] complexes. A second maximum at 338 mμ in the pyridine complex is absent in the keto-substituted pyridine derivatives, being obscured by the strong ultraviolet absorption bands which shift toward the visible when a carbonyl group is placed in conjugation with the pyridine ring. Maxima for the hydroxypyridine complexes lie well beyond those for the aquo (492 mμ) and carboxylate (501–503 mμ) complexes, strongly indicating that these hydroxy ligands are bound to Co(III) at oxygen, rather than at the ring nitrogen.[8]

Kinetic Experiments. Specific rates were determined by following the decrease in optical density at the high-wavelength visible absorption maximum of the cobalt(III) complex in the manner previously described.[2] Acidities were between 0.003 and 1.2 *M*. In most cases ionic strengths were kept at or near 1.3 by addition of $NaClO_4$ or $LiClO_4$, but a number of experiments were carried out at lower ionic strengths, chiefly to assess the effect of ionic strength on reactions of this type. Concentrations were taken so that absorbance changes during the reaction corresponded to greater than one-fourth the total scale of the spectrophotometer chart. For all complexes except the 4-benzoyl derivative, rates were run under pseudo-first-order conditions with the ratio Cr(II)/Co(III) between 10 and 250. In experiments with the very reactive 4-benzoylpyridine complex, the complex (about 3 mg of the perchlorate) was in excess, and very small volumes (10–12 μl) of 0.25 *M* Cr^{2+} were added, using a graduated microsyringe; absorbancy changes here were read on the 0–0.2 slide wire. Temperatures were constant to within better than 0.1° during the entire series of experiments. Reactions were allowed to proceed for at least five half-lives, and, except as indicated below, good first-order plots were obtained. For the slower reactions, not involving the acetyl or benzoyl derivatives, rate constants taken from several points in a single run agreed to better than 6%, and those from different runs checked to about 10%. Specific rates for the 3-acetyl and 3-benzoyl complexes, obtained with more dilute solutions, are less reliable; points within a single run check to within 10% and, between runs, to about 20%. The rate of reduction of the 4-benzoyl complex was measurable only with difficulty at 0° and at very low ionic strengths; the specific rate given is little more than an order of magnitude value. At room temperature reduction of this complex is much too rapid for measurement by these methods.

In the reaction of the acetyl and benzoyl derivatives with excess Cr(II), reduction of Co(III) (which decreases the absorbance at 475 mμ) was followed by two additional reactions, probably successive stages of reduction of the heterocyclic ligand. The first of these increased absorbance and the second decreased absorbance once again. When the reduction was carried out with 0.1 *M* Cr(II) in 1.0 *M* acid, the first two reactions were over very rapidly and the observed drop in absorbance (having a half-life of 15–20 sec under these conditions) was that associated with the third reaction. This difficulty largely disappeared when kinetic experiments were carried out with Cr(II) concentrations less than 10^{-3} *M*, but at high acidities a slight upward drift of absorbance was sometimes observed, introducing some uncertainty into the "infinity" reading.

Stoichiometry Experiments and Ion-Exchange Separations. Competition experiments, in which 0.02-mmole samples of four of the complexes (Table II) in 0.1 *M* $HClO_4$ were treated with 0.015 mmole of Cr(II), were carried out in vials sealed by rubber serum caps as previously described.[2a] With the slowly reacting dimethylnicotinamide complex (VI), the reaction mixture was allowed to stand overnight before analyzing for Co(II); the results in this case appear to have significance only as a lower limit since Cr(II) almost certainly was partially consumed by traces of oxygen slowly diffusing into the vial.

Table II. Yields of Co(II) from Reduction of Substituted Pyridinepentaamminecobalt(III) Complexes[a]

Ligand	Yield of Co(II), %
3-Acetylpyridine	100
3-Benzoylpyridine	100
4-Benzoylpyridine	100
N,N-Dimethylnicotinamide	>56

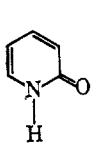
[a] $[H^-]$ = 0.12 *M*; [Co(III)] = 0.02 *M*; [Cr(II)] = 0.014 *M*; Cr(II) added to Co(III).

The Cr(III) product resulting from reduction of the 4-benzoyl and 3-acetyl complexes was separated from solution, using cation-exchange chromatography, and its spectrum taken. For these experiments, 0.02 mmole of the complex in 2.0 ml of 0.1 *M* $HClO_4$ was treated with an equivalent quantity of Cr(II). The resulting solution was then absorbed onto the cation-exchange column (4 ml of resin, pretreated as described above, comprising a 5-in. column) and elution carried out with a solution 1.2 *M* in $NaClO_4$ and 0.02 *M* in $HClO_4$ (elution rate 0.6 ml/min). With both the benzoyl and acetyl complexes, the Cr(III) product, which followed uncharged and unipositive organic species and dipositive cobalt off the column, exhibited a visible spectrum corresponding to that of aquochromic ion.[9] Recovery of Cr(III) was generally good (90–100%). More-

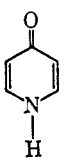
(6) The substituted pyridinecobalt(III) iodides prepared in this study are photosensitive; when dry samples are exposed to light, they rapidly darken, first to green, then to brown. Moreover, in recrystallizing these iodides, care should be taken to minimize thermal decomposition; preparations should not remain above 60° for more than a few minutes. The perchlorates, in contrast to the iodides, appear to be stable indefinitely at room temperature, even in intense light.

(7) Both the large shift in absorption maximum (toward higher energies) and the surprising resistance to hydrolysis indicate significantly stronger binding of Co(III) in these 2-acylpyridine products than in hexaammine- and pyridinepentaamminecobalt(III) complexes. These observations further suggest incorporation of Co(III) into a chelate ring, formed possibly by condensation of cobalt-bound ammonia with the α-keto group.

(8) The extreme ease with which 2- and 4-hydroxypyridine coordinate with Co(III), when contrasted with the difficulty here encountered in preparing the 3-hydroxypyridine complex under a variety of conditions, suggests that the 2 and 4 isomers coordinate *via* their respective "keto" (amide-like) forms (XI and XII); no such form is possible for the 3-hydroxy isomer.



XI



XII

over, in cochromatography experiments, in which a known quantity of $Cr(H_2O)_6^{3+}$ was added, as its perchlorate, to the mixture after reaction, only one Cr(III)-containing band appeared on the column. The products resulting from the more slowly reacting complexes were not examined in this way.

In contrast to results in the carboxamide series,[3] spectra of the reaction mixtures obtained from reduction of the benzoyl and acetyl complexes gave no good indication of the presence of a metastable intermediate. With the 4-benzoyl derivative, the spectrum of the reaction mixture 4 min after reduction was virtually identical with that of the same mixture 5 days after reduction. With the (less pure) 3-acetyl derivative, there was a slow but perceptible diminution in absorbance at 550–600 mμ on standing 5 days after reduction; apparently, non-Cr(III) species are involved here, for ion-exchange chromatography of both the freshly prepared reaction mixture and the 5-day-aged mixture yielded only hexaaquochromium(III).

Reduction of Noncoordinated Ligands. Oxidation–reduction experiments, in which substituted pyridines were treated, in 0.12 *M* $HClO_4$, with Cr(II) and the unreacted Cr(II) was estimated by reaction with excess $(NH_3)_5CoCl(ClO_4)_2$, were carried out as described.[2a]

Results and Discussion

Kinetic data are presented in Table III. The increase in specific rate with ionic strength is as expected for a reaction between two positive ions and is consistent, both in magnitude and direction, with kinetic salt effects reported for the Cr(II) reduction of halopentaamminecobalt(III) derivatives.[10] Considering only values at high μ, it is clear that the specific rates fall into two distinct groups. Values for the keto-substituted pyridine derivatives lie in the range 10^2–10^3 l. mole^{-1} sec^{-1}, whereas the other complexes are reduced at specific rates near 10^{-2}–10^{-3}. Although reduction of the 4-benzoyl compound at room temperature is too rapid to measure by methods available here, an estimate of its rate at 25° and $\mu = 1.2$ may be made by assuming a four- to sixfold increase in rate on changing μ from 0.01 to 1.2 *M* (as is observed with the other keto derivatives) and another two- to fivefold increase resulting from raising the temperature. The value so obtained lies in the range 2000–7000 l. mole^{-1} sec^{-1}; this appears to be the highest specific rate thus far reported for nonchelating reduction of an organic $(NH_3)_5Co$ derivative by Cr(II).[11] Comparing this value with that for the unsubstituted pyridine complex, we see that incorporation of the 4-benzoyl group has boosted the rate of reduction of ring-bound Co(III) by a factor of approximately 10^6, a much more striking effect than the specific rate increases (fivefold to 300-fold) resulting from 2- or 4-carbonyl substitution in the benzoato series.[12] What is perhaps more surprising is that the 3-keto compounds in the present series react almost 10^5 times as rapidly as the unsubstituted pyridine complex, whereas incorporation of a 3-acyl substituent has only a marginal kinetic effect in the benzoato series. Note also that the reduction rates of keto-substituted pyridine derivatives are acid-independent, whereas those for 4-carbonyl-substituted (but not 2-carbonyl-substituted) benzoato derivatives have a first-order hydrogen ion term, which, at high acidities, may account for the major portion of the reaction.

Table III. Kinetic Data for Chromous Reduction of Pentaamminecobalt(III) Complexes

Organic ligand	μ	(H^+), *M*	k^a
Pyridine	1.0	0.08–0.63	0.0039[b]
N,N-Dimethylformamide	1.3	1.20	0.0072
		0.11	0.0075
N,N-Dimethylnicotinamide (VI)	1.3	1.24	0.029
		0.24	0.034
	0.3	0.24	0.016
3-Acetylpyridine (IV)	1.2	1.2	130
		0.12	130
		0.012	120
	0.12	0.12	50
	0.037	0.036	28
	0.013	0.012	25
3-Benzoylpyridine (V)	1.2	1.2	250
		0.12	200
		0.012	190
	0.038	0.037	96
	0.013	0.012	63
	0.005	0.003	31
4-Benzoylpyridine (VII)	0.010	0.010	230 (0°)
	0.003	0.0017	220 (0°)
2-Hydroxypyridine (IX)	1.3	1.2	0.013
4-Hydroxypyridine (VIII)	1.3	1.2	0.024
	1.2	0.24	0.019
		0.12	0.021
Pyrazole (X)	1.3	1.2	0.0023

[a] Specific rates in l. mole^{-1} sec^{-1} at 24.5°. [b] F. Nordmeyer, H. Taube, and A. H. Sargeson, unpublished experiments, Stanford University, 1964.

The present investigation sheds little direct light on the mechanism by which the slower reductions proceed. The reduction of the unsubstituted pyridine complex has been shown to proceed by direct electron transfer without intervention of a bridging group,[13] that is, *via* an "outer-sphere" activated complex; it is probable that the pyrazole complex, which reacts even more slowly, takes this path also. The other reductions in the "slow" group appear to lie in the range of values where outer-sphere reduction and reduction *via* ligand transfer compete, provided that a suitable site is available for the latter. Such competition has been convincingly demonstrated for reduction of the 3-carboxamidopyridine (nicotinamide) derivative (II), for which reduction *via* ligand transfer ($k = 0.032$) proceeds 2.5 times as rapidly as direct electron transfer ($k = 0.013$ l. mole^{-1} sec^{-1} at 25°);[3] a corresponding duality of mechanism may apply to reduction of the N,N-dimethylated carboxamide derivative in the present series, possibly with a lesser contribution from ligand transfer. The DMF complex and the "amide-like" complexes of 2- and 4-hydroxypyridine have the structural elements which could, in principle, allow reduction *via* a bridged activated complex, but such a path for O-coordinated

(9) J. A. Laswick and R. A. Plane, *J. Am. Chem. Soc.*, **81**, 3564 (1959).

(10) J. P. Candlin and J. Halpern, *Inorg. Chem.*, **4**, 766 (1965).

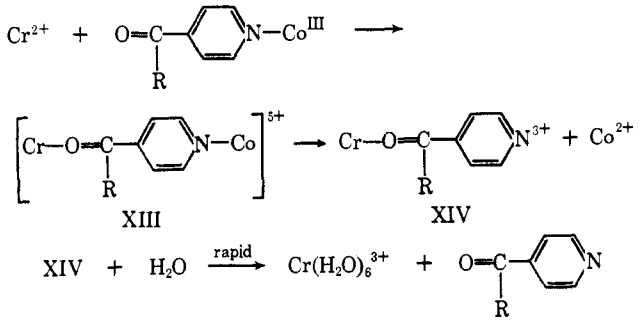
(11) Other organic ligands that greatly accelerate Cr(II) reduction of bound $Co(NH_3)_5$ are pyridine-2-carboxylato (k = 20,000), pyrazinecarboxylato ($k > 1100$), and salicylato (k for the nonprotonated form = 2×10^8) (rates in l. mole^{-1} sec^{-1} at 25°[2]). Each of these has a basic site in a position favorable for chelation at the attacking Cr(II). There is strong evidence that the first two of these complexes form chelated Cr(III) products, but the structure of the Cr(III) product(s) resulting from the salicylato complex has not been satisfactorily established.

(12) The largest specific rate increases (about 300-fold) for reductions in the benzoato series have been observed for the 2- and 4-formyl (aldehydo) derivatives,[2] the pyridine analogs of which were not preparable by the present methods. Acceleration due to acetyl or benzoyl substitution in the benzoato series is even more modest. Indeed, the acid-independent term for reduction of the 4-benzoylbenzoato complex (the benzoate complex most directly comparable to the 4-benzoylpyridine complex) is only about twice that for the unsubstituted benzoato derivative, and participation of the 4-benzoyl group in the reduction of the benzoylbenzoato complex would probably be overlooked were it not for the acid-dependent term in the rate law and the formation of free benzoylbenzoic acid (rather than its Cr(III) complex) in the reaction.[2a]

(13) F. Nordmeyer and H. Taube, unpublished results.

amides has not yet been demonstrated. This problem is being pursued in these laboratories.

A clearer picture emerges for the rapid reduction of the acetyl and benzoyl derivatives. The isolation of $Cr(H_2O)_6^{3+}$ as the sole Cr(III) product in these cases is consistent either with reaction through an outer-sphere activated complex, or, alternatively, with a mechanism featuring Cr(II)–oxygen bond formation at the keto group (XIII) and electron transfer through the organic ligand to N-bound cobalt (reduction by "remote attack"), followed by rapid hydrolysis of XIV, the keto-bound Cr(III) product.[14] However, the very large rate in-



creases resulting from incorporation of keto groups in this series argue strongly for the latter mechanism, for it is difficult in the extreme to see how such substituents, far removed from the Co(III) center, can so drastically affect reduction rates without themselves becoming involved in the electron-transfer process, thus changing the reaction mechanism. The absence of a term first order in hydrogen ion in the rate laws for reduction of the keto complexes here is consistent with formulation VI, for in this structure (unlike the corresponding intermediate for remote attack in the benzoate series) there are no donor sites available for coordination with H^+.

In attempting to account for the remarkably large rate enhancements resulting from keto substitution into Co(III)-bound pyridine, in contrast to the effects observed with Co(III)-bound benzoate, several factors may be considered. First, and probably most important, carbonyl substitution in the pyridine ligand introduces an electron bridge into a system which had none, whereas such substitution in a benzoato ligand merely introduces a second (perhaps slightly more favorable) bridging path into a system already having one. Secondly, as data on the reduction of the noncoordinated ligands (Table IV) emphasize, substituted pyridines are

(14) Hydrolysis of a keto–chromium species such as XIV would be expected to proceed by carbon–oxygen, rather than by chromium–oxygen, bond breakage. Ligand substitutions about Cr(III) centers in acidic aqueous solutions are almost always slow at room temperature (see, for example, R. E. Hamm, R. L. Johnson, R. H. Perkins, and R. E. Davis, *J. Am. Chem. Soc.*, **80**, 4469 (1958)). On the other hand, substitution reactions by water, in such solutions at $>C^+-OH$ centers (which are structurally analogous to $>C{=}O{-}Cr^{3+}$), are generally rapid and, in a number of cases, have been shown to be virtually complete in a few seconds or less. See, for example, M. Cohn and H. C. Urey, *ibid.*, **60**, 679 (1938); R. P. Bell and J. C. Clunie, *Proc. Roy. Soc.* (London), **211A**, 254 (1952); M. L. Ahrens and H. Strehlow, *Discussions Faraday Soc.*, **39**, 112 (1965).

Table IV. Reduction of Noncoordinated Donors with Cr(II)

Substrate	Reducing agent consumed, %	Color produced
Heterocyclic Donors[a]		
Pyridine	25	
Quinoline	19	
Pyrazole	20	
N,N-Dimethylnicotinamide	23	
3-Cyanopyridine	21	
4-Cyanopyridine	44	
3-Acetylpyridine	11	
3-Benzoylpyridine	32	
4-Acetylpyridine	88	Yellow
4-Benzoylpyridine	93	Brown
4-Pyridinecarboxylic acid[b]	>40	Purple
Pyrazine	58	Green[c]
Benzoic acids[b]		
Benzoic	0	
4-Formylbenzoic	0	
4-Benzoylbenzoic	5	
2-Acetylbenzoic	0	

[a] 30 min, 25°, 0.12 *M* $HClO_4$, concentration of donor 3.0 g/l., (Cr^{2+}) 0.01 *F*. [b] 40 min, 25°, 0.15 *M* $HClO_4$, concentration of organic acid 4.0 g/l., (Cr^{2+}) 0.01 *F* (see ref 2a). [c] Green color faded within a few minutes and light green precipitate formed.

reduced by Cr(II) considerably more readily than are the correspondingly substituted benzoic acids. The comparison is pertinent in view of growing evidence[2,15] that the most effective bridging groups for electron tranfers of this type are those which are themselves reducible by Cr^{2+} and which have, at the same time, a path through which such transfer may occur. An additional difference between the 4-benzoyl derivatives in the two series is that the benzoyl group is in direct conjugation with the Co(III)-bound nitrogen in the pyridine derivative, whereas the Co(III)-bound oxygen in the benzoato derivative is separated from the conjugated system by a pair of adjacent single bonds (ArCOOCo).[16]

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(15) E. S. Gould, *J. Am. Chem. Soc.*, **88**, 2983 (1966).

(16) This difference in conjugative relationships is of less consequence than might be anticipated on the basis of previous experience[2a] with reduction of the various pyridinecarboxylato derivatives, for in the present series the "improperly conjugated" 3-keto substituents (having an odd, rather than an even, number of atoms connecting the cobalt-bound nitrogen and the carbonyl oxygen) are associated with rate increases of five powers of ten; only a single order of magnitude separates specific rates for the 3-keto complexes from that for the directly conjugated 4-benzoyl complex. Moreover, if the energies of activation for these reductions resemble the respective values for the corresponding carboxamide derivatives,[13] specific rate differences for the keto-substituted isomers will become even less at higher temperatures. The presence of the keto substituent is thus more important than is its location in facilitating reduction.