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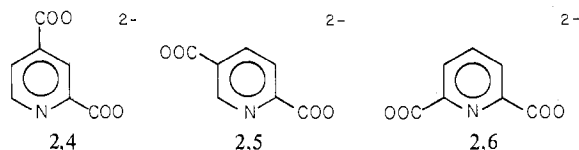
Electron Transfer through Organic Structures. 37. Mediation of Chromium(II) Reductions by Bound Pyridinedicarboxylate Groups in Which the Coordination Position is Directed¹

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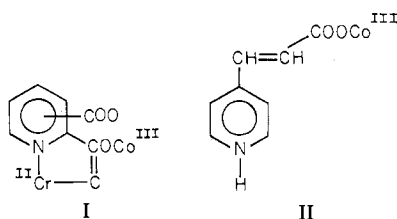
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The reductions, using Cr^{2+} , of 2,3-, 2,4-, and 2,5-pyridinedicarboxylate derivatives of $(\text{NH}_3)_5\text{Co}^{\text{III}}$, in which coordination is directed specifically, by blocking, either to the 2 position or to the position more remote from the ring nitrogen, are compared. Rate laws for reductions of both the 2-substituted and the remotely substituted complexes exhibit prominent inverse-acid terms, and for all 2,4 and 2,5 derivatives examined, only this term is observed. Although the form of the rate law is thus not indicative of the position of coordination, the specific rates for the 2-COOCO complexes are found to be 10^1 – 10^4 as great as those for the corresponding distantly coordinated complexes. Moreover, rates for the 2-COOCO oxidants lie very near those for the unblocked dicarboxylate complexes prepared by direct ligation of the free diacids. Observed differences in the spectra of the chromium(III) products from the various reductions are consistent with the expected formation of chelated products from the 2-coordinated oxidants and nonchelated products from the remotely coordinated oxidants. Rates for the 3-, 4-, and 5-COOCO oxidants, although lower than those for the 2-COOCO oxidants, greatly exceed those for ordinary aliphatic and aromatic carboxylate complexes. In order to reconcile the kinetic inverse-acid dependencies observed for the nonchelating oxidants with earlier proposals that such complexes are reduced via preliminary one-electron reduction of the ring to a metal-bound radical, a sequence is suggested in which the rate of net reaction depends not only on the rate of formation of the radical intermediate but also on the rate at which the reducing electron migrates from ligand to cobalt(III). Whether this passage is assisted or retarded by protonation of the intermediate appears to depend on the location of the protonation site in relation to the electron-transfer path.

Although studies in the early 1960's demonstrated the remarkable effectiveness of 2,4- and 2,5-pyridinedicarboxylate in the mediation of electron transfer to bound cobalt(III),² it was recognized that interpretation of this action was ambiguous. In contrast to the 2,6 isomer, which features two



equivalent COOH groups, the 2,3, 2,4, and 2,5 ligands may coordinate at the 2 position, at a position more distant from the ring nitrogen, or at both sites. In a typically perplexing instance, it was originally proposed,³ on the basis of $\text{p}K_a$ comparisons, that ligation of the 2,5 isomer with $(\text{NH}_3)_5\text{Co}^{\text{III}}$ gave a 5-substituted complex, but later studies^{2b,4} suggested instead that this ligand, and the 2,3 and 2,4 isomers as well, coordinated preferentially at the 2 position. A key point in this reassessment was the belief (based on examination of monocarboxylate systems) that the observed very rapid reactions of the resulting cobalt(III) complexes with Cr^{2+} , at rates inversely proportional to (H^+) , proceeded through a chelated intermediate of type I and were therefore diagnostic of 2-coordination. This argument, however, was seriously weakened by the later finding⁵ that Cr^{2+} reductions of nonchelating pyridylacrylate complexes such as II proceeded at significantly enhanced specific rates and likewise featured rate laws having prominent $(\text{H}^+)^{-1}$ terms.



The present work deals with reductions of $(\text{NH}_3)_5\text{Co}^{\text{III}}$ complexes of pyridinedicarboxylic acids in which either the 2-carboxyl or the carboxyl more remote from nitrogen is

blocked off by conversion to an ester or amide function, allowing an unambiguous mode of coordination. Our results support the proposal of preferential 2-coordination by the unblocked diacids but, somewhat paradoxically, show that the argument which was used in justification was inadmissible.

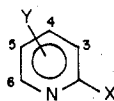
Experimental Section

Materials. Aquopentaamminecobalt(III) perchlorate,^{2a} lithium perchlorate,^{4a} and solutions of $\text{Cr}(\text{II})^{2a}$ and $\text{Eu}(\text{II})^6$ were prepared as described. Nitrosyl perchlorate was prepared, in a modification of the method of Brauer,⁷ by treating 70% HClO_4 at 0 °C with a mixture of NO and NO_2 . Isomeric pyridinedicarboxylic acids and *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide (for preparation of diazomethane⁸) were Aldrich products and were used as received. An alternate source of 2,4-pyridinedicarboxylic acid, K&K Technical Grade, required three recrystallizations from hot water before giving satisfactory results.

Preparation of Blocked Ligands. Interconversions among pyridinedicarboxylate derivatives were carried out principally as described by Thunus and Dejardin-Duchens.⁹ One set of conversions, pertaining to the 2,3-dicarboxylate series, is summarized in Scheme I. Parallel sequences were carried out in the 2,4 and 2,5 series.¹⁰ For deamination of the carbomethoxyamide IV to the corresponding half ester (and for the analogous 2,4 and 2,5 transformations), cautious treatment with nitrosyl perchlorate in trimethyl phosphate¹¹ was found to be more effective than the action of sodium nitrite in HCl, as recommended by Thunus. Attempted regiospecific conversions in the 2,3 series using the procedures of Kirpal¹² and Kenyon and Thaker¹³ were not successful.

Preparation of the Complexes. Complexes from the more soluble acids were prepared from aquopentaamminecobalt(III) perchlorate in water,^{2a} whereas those from less soluble acids were obtained from the corresponding carbonato nitrate^{2a} in diethylene glycol^{4a} as described. Although ligation generally proceeded without difficulty, the resulting complexes were often contaminated with the parent acids which, particularly in the 2,4 and 2,5 series, were but sparingly soluble in water. In a modified method of purification, which was found to be greatly superior to treatment with NaHCO_3 ,^{2a} the impure complex was carefully dissolved in an aqueous solution of tris(hydroxymethyl)aminomethane (1–2 M) at room temperature, after which the complex was quickly precipitated by addition of aqueous NaClO_4 and then recrystallized from hot water.¹⁴ Amide-substituted complexes were converted to COOH-substituted derivatives by careful treatment with NOClO_4 .^{11,15} Analyses of purified complexes are listed in Table I.

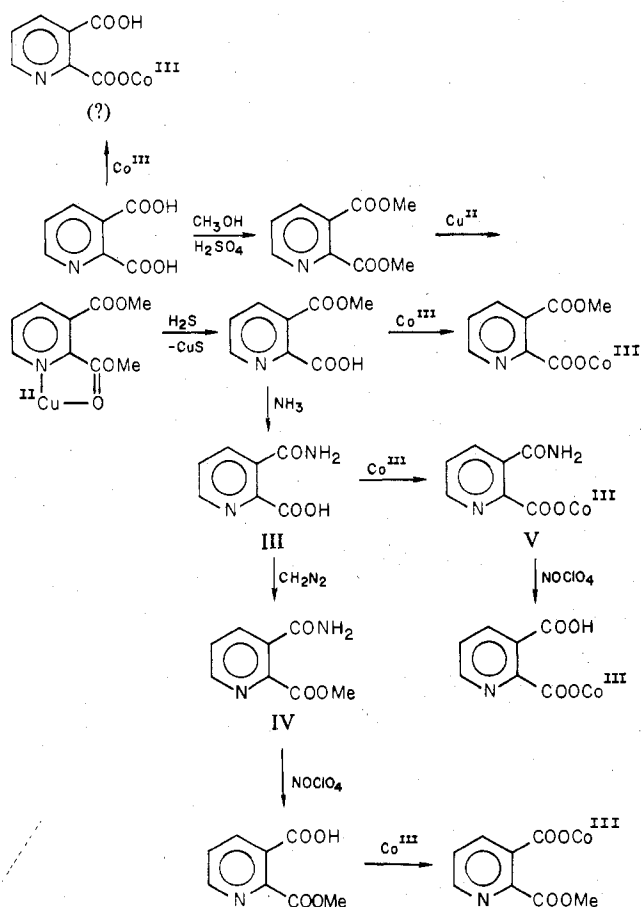
Table I. Analyses of (Pyridinedicarboxylato)pentaamminecobalt(III) Perchlorates



ring substituents		% C		% H		% Co	
X	Y	calcd	found	calcd	found	calcd	found ^a
2-COOC _o (NH ₃) ₅	6-COOCH ₃	18.36	18.21	4.21	4.13	11.28	11.25
2-COOC _o (NH ₃) ₅	6-CONH ₂	16.56	16.30	3.94	4.04	11.59	11.08
2-COOC _o (NH ₃) ₅	5-COOCH ₃	18.36	18.38	4.21	4.11	11.28	11.30
2-COOC _o (NH ₃) ₅	5-CONH ₂	16.56	16.79	3.94	4.10	11.59	11.46
2-COOCH ₃	5-COOC _o (NH ₃) ₅	18.36	18.27	4.21	4.15	11.28	11.07
2-COOC _o (NH ₃) ₅	4-CONH ₂	16.56	16.35	3.94	4.03	11.59	11.12
2-COOCH ₃	4-COOC _o (NH ₃) ₅	18.36	18.39	4.21	4.19	11.28	11.22
2-COOC _o (NH ₃) ₅	3-COOCH ₃	18.36	18.28	4.21	4.15	11.28	11.40
2-COOC _o (NH ₃) ₅	3-CONH ₂	16.56	16.48	3.94	3.91	11.59	11.43
2-COOCH ₃	3-COOC _o (NH ₃) ₅	18.36	18.26	4.21	4.05	11.28	11.40
2-COOC _o (NH ₃) ₅ ^b	3-COOH					11.58 ^c	11.26
2-COOC _o (NH ₃) ₅ ^b	5-COOH					9.67 ^d	9.46

^a See ref 2a. ^b Prepared by action of NOClO₄ on the CONH₂-substituted complex.¹¹ ^c % N 16.26 (calcd 16.51). ^d Tris perchlorate. % N 13.55 (calcd 13.79).

Scheme I



Kinetic Experiments. Specific rates were estimated from measurements of absorbance changes at 502 nm. Most experiments were carried out with the Durrum-Gibson stopped-flow spectrophotometer as described,^{4b} but a few of the slower reactions were studied on the Cary spectrophotometer using conventional mixing methods. All reactions were first order each in Co(III) reductant, but rate measurements employed pseudo-first-order conditions with at least a fivefold excess of reductant. Rates were strongly dependent on acidity in the range 0.12–1.2 M H⁺. Ionic strengths were adjusted to 1.2 M with twice-recrystallized LiClO₄. Replicate reactions, with the same pair of master solutions, were carried out until absorbance curves for three consecutive runs superimposed. Rate constants, obtained from logarithmic plots of absorbance differences against reaction time,

agreed to better than 6% for runs with different master solutions, provided that half-life periods were 10 ms or greater. For faster reactions, reproducibility between runs was poorer. Temperatures were kept at 25.0 ± 0.2 °C during the entire series of experiments. Reductions, with Eu²⁺, of the various 2,3, 2,4, and 2,5 derivatives exhibited autocatalytic behavior analogous to that already noted with a number of additional pyridine derivatives,^{6,16} but kinetic curves conforming to straightforward pseudo-first-order behavior were obtained with the 2,6 complexes.

Spectra of the Products. The visible spectra of the chromium(III) products formed in the reductions with Cr²⁺ were taken by adding successive known quantities of reductant to excess oxidant and then subtracting the known absorbancies of the Co(III) complex remaining and Co²⁺ formed.¹⁷ Agreement between spectra calculated at various stages of such titrations was good, and isosbestic points were observed in each case. The positions of absorption maxima and isosbestic points and the calculated molar absorbancies were very nearly independent of acidity in the range 0.12–1.2 M H⁺.

Results and Discussion

Kinetic data appear in Table II. Reactions with chromium(II) in the 2,3, 2,4, and 2,5 series are acid dependent, with all reductions except that of the 2-COOCH₃-3-COOC_o^{III} complex adhering closely to an inverse-H⁺ rate law in the range of 0.12–1.2 M H⁺. Kinetic parameters derived from these data are summarized in Table III. Since the predominant cobalt(III) species within the pH interval examined is the N-protonated tripositive form in each instance,^{18,19} the observed (H⁺)⁻¹ dependencies point to a transition state with a composition corresponding to Cr^{II}·Co_B (where "Co_B" represents the nonprotonated dipositive form of the oxidant) for the principal reduction path. This inverse-acid component is seen to be important for those oxidants in which Co(III) is attached to the "remote" position, as well as for the 2-COOC_o^{III} oxidants. Hence, the form of the rate law is not indicative of the position of coordination.

The magnitudes of the specific rates for the inverse-acid paths (*k*₋₁ values, Table III) appear to be more informative, for these are 10¹–10⁴ times as great for the 2-COOC_o complexes as for the more remotely coordinated oxidants. More important, *k*₋₁ values for the unblocked dicarboxylato complexes, prepared earlier by direct ligation of the dicarboxylic acids, are found to lie near the corresponding terms of the 2-COOC_o complexes, being, at the same time, much greater than those for the 3-, 4-, and 5-COOC_o derivatives. In addition, the kinetic characteristics of the 2-COOC_o-3-COOH oxidants prepared by unequivocal routes via deamination of the respective CONH₂-substituted complexes are seen (Table II) to correspond closely to those of the complexes

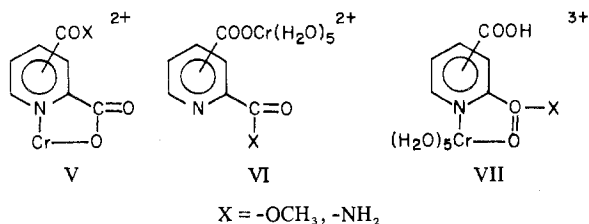
Table II. Kinetic Data for Reductions of Pentaamminecobalt(III) Complexes of Dicarboxylatopyridines^a

ring substituents	reductant	(H ⁺), M	k
2-COOC _o (NH ₃) ₅ , 3-COOCH ₃	Cr(II)	0.12	51 × 10 ²
		0.24	22 × 10 ²
		1.2	5.9 × 10 ²
2-COOC _o (NH ₃) ₅ , 3-CONH ₂		0.12	10.7 × 10 ³
		0.24	5.1 × 10 ³
		0.60	2.4 × 10 ³
2-COOCH ₃ , 3-COOC _o (NH ₃) ₅ ^b		0.12	0.79
		0.24	0.67
		0.50	0.55
		0.75	0.51
		1.2	0.48
2-COOC _o (NH ₃) ₅ , 3-COOH ^c		0.24	35 × 10 ²
		1.20	7.9 × 10 ²
2-COOC _o (NH ₃) ₅ , 3-COOH ^d		0.24	33 × 10 ²
		1.20	7.0 × 10 ²
2-COOC _o (NH ₃) ₅ , 4-CONH ₂		0.24	41 × 10 ³
		1.20	9.1 × 10 ³
2-COOCH ₃ , 4-COOC _o (NH ₃) ₅		0.12	34 × 10 ²
		0.24	13 × 10 ²
		0.60	5.7 × 10 ²
		1.20	3.3 × 10 ²
		1.20	29 × 10 ³
2-COOC _o (NH ₃) ₅ , 5-COOCH ₃		0.24	12.6 × 10 ³
		1.20	2.9 × 10 ³
		1.20	7.5 × 10 ²
2-COOCH ₃ , 5-COOC _o (NH ₃) ₅		0.24	3.3 × 10 ²
		0.60	1.25 × 10 ²
		1.20	0.76 × 10 ²
2-COOC _o (NH ₃) ₅ , 5-COOH ^e		0.24	7.1 × 10 ³
		1.20	1.7 × 10 ³
2-COOC _o (NH ₃) ₅ , 5-COOH ^d		0.24	8.2 × 10 ³
		1.20	2.0 × 10 ³
2-COOC _o (NH ₃) ₅ , 6-COOCH ₃		0.12	27 × 10 ³
		0.24	13 × 10 ³
		1.20	2.9 × 10 ³
2-COOC _o (NH ₃) ₅ , 6-CONH ₂		0.24	4.0 × 10 ⁴
		1.20	3.8 × 10 ⁴
2-COOC _o (NH ₃) ₅ , 4-CONH ₂	Eu(II)	1.20	1.2 × 10 ^{3 f}
		0.12	10.5 × 10 ³
2-COOC _o (NH ₃) ₅ , 6-COOCH ₃		1.20	5.0 × 10 ³
		0.12	5.8 × 10 ³
2-COOC _o (NH ₃) ₅ , 6-CONH ₂		1.20	4.6 × 10 ³

^a Specific rates in M⁻¹ s⁻¹ at 25 °C; μ = 1.2. (Co^{III})₀ = 0.001; (Cr^{II}) = 0.005-0.05. ^b Values determined on the Cary spectrophotometer. ^c Complex prepared by action of the 2,3-dicarboxylic acid on H₂O(NH₃)₂Co³⁺.^{2a} A second (minor) component exhibited specific rates near 1 × 10² M⁻¹ s⁻¹ (1.2 M H⁺) and 2 × 10² M⁻¹ s⁻¹ (0.6 M H⁺). ^d Complex prepared by the reaction of NOClO₄ with the CONH₂-substituted complex.¹¹ ^e From the reaction of the 2,5-dicarboxylic acid with H₂O(NH₃)₅Co³⁺.^{2a} A second (minor) component exhibited a specific rate near 90 M⁻¹ s⁻¹ (1.2 M H⁺). ^f Autocatalytic reaction; specific rate calculated from initial rate.

prepared from the unblocked diacids.

Spectral characteristics of the chromium(III) products formed in the Cr²⁺ reductions are summarized in Table IV. Comparisons are possible in the 2,4 and 2,5 series, in which it is found that the products from the 2-COOC_o complexes absorb at higher energies and exhibit greater extinction coefficients than those from the corresponding remote-substituted oxidants. Both trends are consistent with the formation of chelated products of type V (in which one of the ligating

**Table III.** Kinetic Parameters for Chromium(II) Reductions of Pentaamminecobalt(III) Complexes of Dicarboxylatopyridines:^a rate = [Cr^{II}][Co^{III}]/[k₋₁(H⁺) + k₀]

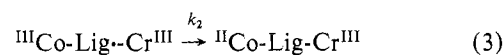
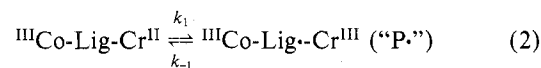
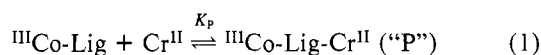
ring substituents	k ₋₁	k ₀
2-COOC _o (NH ₃) ₅ , 3-COOCH ₃	6.2 × 10 ²	
2-COOC _o (NH ₃) ₅ , 3-CONH ₂	1.2 × 10 ³	
2-COOCH ₃ , 3-COOC _o (NH ₃) ₅	0.04	0.46
2-COOC _o (NH ₃) ₅ , 4-CONH ₂	1.0 × 10 ⁴	
2-COOCH ₃ , 4-COOC _o (NH ₃) ₅	4.1 × 10 ²	
2-CONH ₂ , 4-COOC _o (NH ₃) ₅	~10 ^{3 b}	
2-COOC _o (NH ₃) ₅ , 5-COOCH ₃	3.5 × 10 ³	
2-COOCH ₃ , 5-COOC _o (NH ₃) ₅	91	
2-COOC _o (NH ₃) ₅ , 6-COOCH ₃	2.3 × 10 ³	
2-COOC _o (NH ₃) ₅ , 3-COOH ^c	6.7 × 10 ²	1.9 × 10 ³
2-COOC _o (NH ₃) ₅ , 4-COOH ^c	2.6 × 10 ⁴	7.3 × 10 ⁴
2-COOC _o (NH ₃) ₅ , 5-COOH ^c	1.3 × 10 ³	2.0 × 10 ³
2-COOC _o (NH ₃) ₅ , 6-COOH ^c	1.5 × 10 ⁴	

^a Reactions at 25 °C, μ = 1.2. ^b Estimated as twice the value for the 2-COOCH₃, 4-COOC_o^{III} complex. ^c Values adjusted for partial conversion of these oxidants to unreactive protonated (tri-positive) forms.^{4b}

atoms is nitrogen) from the 2-coordinated oxidants but nonchelates of type VI (in which all six ligating atoms are oxygen) from the 4- and 5-COOC_o complexes.²⁰ The differences, however, are small and do not, in themselves, convincingly rule out formation of chelates of type VII from the remote oxidants, but the latter possibility must be considered extremely unlikely in view of recent evidence⁵ that Cr²⁺ reductions of COOC_o^{III} derivatives of pyridine proceed by electron transfer through the coordinated carboxyl, even when the pyridine nitrogen lies in conjugation with the Co(III) center.²¹

This work thus confirms the earlier view that 2,3-, 2,4-, and 2,5-pyridinedicarboxylic acids undergo ligation with Co(III) preferentially at the 2 position and that the resulting 2-COOC_o^{III} complexes are reduced by Cr²⁺ via chelated activated complexes. At the same time, we have demonstrated that 3-, 4-, and 5-COOC_o^{III} oxidants in this series are also reduced much more rapidly than ordinary aliphatic, alicyclic, and aromatic carboxylato derivatives of (NH₃)₅Co^{III} and that these reductions, like those of the 2-COOC_o complexes, feature strong, sometimes predominant, inverse-H⁺ kinetic components. Arguments have been presented⁵ that the high reduction rates of 2-COOC_o derivatives reflect mainly increases in the association constants of the Co(III)-Cr(II) precursor complexes (such as I) resulting from chelation, but the enhanced rates observed for the remotely substituted oxidants obviously cannot be rationalized in this fashion. The ligands examined here are closely related to those for which the "chemical" or "radical ion" mechanism was proposed,^{2a,3} and this mechanistic variation should be considered for the remotely substituted oxidants in the present series as well.

As indicated, this sequence includes two acts of electron transfer, the first from reductant to ligand in the precursor, P, yielding a radical intermediate bound to two metal centers, P[•], followed by a second transfer from the radical center to cobalt(III):



An analogous sequence can be written for a possible protonated path utilizing this type of mechanism. Application of the

Table IV. Spectra of the Chromium(III) Products from Chromium(II) Reductions of Pentaamminecobalt(III) Complexes of Dicarboxylatopyridines

ring substituents	(H ⁺), M	λ_{\max} , nm	ϵ_1	λ_{\max} , nm	ϵ_2	isosbestic points, nm
2-COOC _o (NH ₃) ₅ , 3-COOCH ₃	0.12	400	45.1	546	37.4	324, 376, 437, 547
	1.20	402	48.8	544	39.9	325, 375, 435, 540
2-COOC _o (NH ₃) ₅ , 3-CONH ₂	0.12	401	43.4	545	35.1	325, 375, 438, 543
	1.20	403	39.7	545	37.1	326, 374, 438, 543
2-COOC _o (NH ₃) ₅ , 4-CONH ₂	0.12	405	40.9	538	33.8	369, 445, 536
		407	30.0	558	28.9	383, 434, 554
2-COOCH ₃ , 4-COOC _o (NH ₃) ₅		402	43.9	544	35.9	374, 438, 554
2-COOC _o (NH ₃) ₅ , 5-COOCH ₃		406	30.5	551	28.4	379, 438, 551
2-COOCH ₃ , 5-COOC _o (NH ₃) ₅		422	40.4	573	71.8	383, 452, 527
2-COOC _o (NH ₃) ₅ , 6-COOCH ₃		418	43.8	587	74.0	380, 450, 533
2-COOC _o (NH ₃) ₅ , 6-CONH ₂						

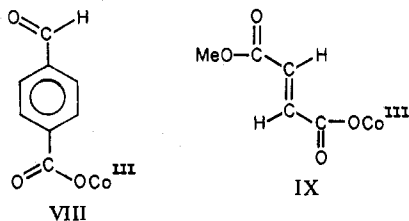
steady-state approximation to the radical intermediates, P, in both paths²² leads to the rate law

$$\frac{\text{rate}}{(\text{Cr}^{2+})} = (\text{Co}_{\text{HB}}) \left[\frac{K_P k_1}{1 + k_{-1}/k_2} \right]_{\text{HB}} + (\text{Co}_{\text{B}}) \left[\frac{K_P k_1}{1 + k_{-1}/k_2} \right]_{\text{B}} \quad (4)$$

in which (Co_{HB}) and (Co_B) represent concentrations of the protonated and deprotonated oxidants and the K_P and k values in brackets refer to the paths indicated by the accompanying subscripts. The manner in which reaction rate responds to changes in acidity then depends upon which of the two composite bracketed expressions in (4) is the greater.

Although the value of K_P , the stability constant for the precursor, would be expected, on the basis of electrostatic considerations alone, to be larger for the deprotonated path, this type of difference is known to be far too small in nonchelating situations to account for the trends observed in this study.²³ At the same time, it is recognized that protonation of a conjugated organic species substantially increases the ease with which it accepts an electron from an external reductant,²⁴ i.e., the ratio k_1/k_{-1} must be greater for the protonated component. We may then infer that the strong retardation by H⁺ observed here for each of the nonchelating oxidants reflects mainly a marked decrease in k_2 , the specific rate of internal electron transfer to cobalt(III), on protonation. If this be so, the steady-state concentration of the radical-ion intermediate, P, intervening in the protonated path is much greater than that of its deprotonated counterpart, for the protonated species is formed more rapidly but is consumed more slowly.

It is perhaps instructive to compare the reactions of the nonchelating pyridine complexes in this study to those of the 4-aldehydobenzoate (VIII) and methylfumarate (IX) derivatives of (NH₃)₅Co^{III} described earlier.^{25,26} Considerable



evidence has been presented that Cr²⁺ reductions of the latter are initiated principally by attack at the remote carbonyl function. Moreover, the ease with which these ligands are known to undergo one-electron reduction has been taken to indicate a radical-ion mechanism for these reactions as well,²⁵ although in contrast to those in the present series, they are markedly accelerated by protonation. Applying eq 4, we may again assume K_P to decrease very slightly and k_1/k_{-1} to increase significantly on protonation (which in these instances occurs at the carbonyl group adjacent to bound cobalt(III)).

We suspect then that the carbonyl-related oxidants and the nonchelating pyridine complexes exhibit differing (H⁺) dependencies as a result of opposing responses to protonation by k_2 , the specific rate of intramolecular electron transfer from the radical center to Co(III), and that these in turn reflect differences in the location of the protonation site in relation to the electron-transfer path within the intermediate. Protonation of oxidants VIII and IX at a site near the electron-transfer terminus may be thought to ease the migration of the reducing electron into the coordinated carboxyl group, whereas protonation of the pyridine complexes at the hetero nitrogen, which lies more remote from that terminus, tends to delay electron passage from the ring.

Registry No. Cr(II), 22541-79-3; Eu(II), 16910-54-6; 2-COOC_o(NH₃)₅-3-COOCH₃-C₅H₃N²⁺, 67598-19-0; 2-COOC_o(NH₃)₅-3-CONH₂-C₅H₃N²⁺, 67598-20-3; 2-COOCH₃-3-COOC_o(NH₃)₅-C₅H₃N²⁺, 67598-25-8; 2-COOC_o(NH₃)₅-3-COOH-C₅H₃N²⁺, 67598-28-1; 2-COOC_o(NH₃)₅-4-CONH₂-C₅H₃N²⁺, 67598-21-4; 2-COOCH₃-4-COOC_o(NH₃)₅-C₅H₃N²⁺, 67598-26-9; 2-COOC_o(NH₃)₅-5-COOCH₃-C₅H₃N²⁺, 67598-22-5; 2-COOCH₃-5-COOC_o(NH₃)₅-C₅H₃N²⁺, 67598-27-0; 2-COOC_o(NH₃)₅-5-COOH-C₅H₃N²⁺, 67598-29-2; 2-COOC_o(NH₃)₅-5,6-COOCH₃-C₅H₃N²⁺, 67598-24-7; 2-COOC_o(NH₃)₅-5,6-CONH₂-C₅H₃N²⁺, 67632-51-3; 2-CONH₂-4-COOC_o(NH₃)₅-C₅H₃N²⁺, 67662-32-2; 2-COOC_o(NH₃)₅-4-COOH-C₅H₃N²⁺, 67662-33-3; 2-COOC_o(NH₃)₅-6-COOH-C₅H₃N²⁺, 67662-34-4; V (2-COOCr(OH₂)₄-3-COOCH₃), 67662-35-5; V (2-COOCr(OH₂)₄-3-CONH₂), 67662-36-6; V (2-COOCr(OH₂)₄-4-CONH₂), 67662-37-7; VI (2-COOCH₃-4-COOCr(OH₂)₅), 67662-38-8; V (2-COOCr(OH₂)₄-5-COOCH₃), 67662-39-9; VI (2-COOCH₃-5-COOCr(OH₂)₅), 67662-40-2; V (2-COOCr(OH₂)₄-6-COOCH₃), 67662-41-3; V (2-COOCr(OH₂)₄-6-CONH₂), 67662-42-4.

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- (14) Although the complexes in the present study all undergo hydrolysis, with precipitation of Co₂O₃ in basic solution, rates vary greatly. The 3-COOCH₃-2-COOC_o^{III} complex may be dissolved in 1 M "Tris" at 75

- °C and then recovered by adding aqueous NaClO₄ and quickly cooling.
- (15) This conversion in the 2,3 series proceeded easily with equivalent quantities of the carboxamido complex and NOClO₄ in trimethyl phosphate at 0 °C. The less soluble 4- and 5-CONH₂ complexes required a 50% excess of NOClO₄ and reaction periods of several hours. Deaminated complexes were recovered from the reaction mixtures by dilution with water, extraction of the Me₃PO₄ with ether, and addition of NaClO₄ to the aqueous phase.
 - (16) (a) C. Norris and F. Nordmeyer, *J. Am. Chem. Soc.*, **93**, 4044 (1971); (b) J. R. Barber, Jr., and E. S. Gould, *ibid.*, **93**, 4045 (1971); (c) E. R. Dockal and E. S. Gould, *ibid.*, **94**, 6673 (1972); (d) J. C. Chen and E. S. Gould, *ibid.*, **95**, 5539 (1973).
 - (17) Reduction of the 2-COOMe-3-COOC^{III} complex was so slow that the intervention of secondary reactions (possibly associated with reduction of the heterocyclic ring) led to extremely erratic values for the apparent absorbances of the product obtained from this derivative.
 - (18) We estimate the pK_A values for the protonated forms of the blocked cobalt(III) complexes in the present study to be ~2.5, i.e., 2 pK values below¹⁹ that for the monofunctional 2-COOC^{III} complex, for which a pK_A of 4.49 has been reported.^{2a} The limited solubilities of these complexes in water at room temperature appear to rule out experimental determinations of pK_A's by partial titration. The visible and near-UV spectra of the protonated and nonprotonated forms are not sufficiently different to allow spectrophotometric determinations.
 - (19) See, for example, R. W. Green and H. K. Tong, *J. Am. Chem. Soc.*, **78**, 4896 (1956).
 - (20) The comparison is complicated by the high values of λ_{max} observed for the 2,6 Cr(III) products (Table IV), which are doubtless chelated. No convincing rationale for the position or intensity of the low-energy maxima for such complexes has yet appeared. It is likely, however, that the normally octahedral bond angles about Cr(III) are substantially distorted in such derivatives, reflecting the severe steric requirements of the 2,6 ligands, and partially relaxing Laporte restrictions. A reviewer suggests the possibility of tridentate chelation in these 2,6 Cr(III) products. Although such chelation by ligands closely related to the present systems is known (see, for example, J. D. Curry and D. H. Busch, *J. Am. Chem. Soc.*, **86**, 592 (1964)), examination of molecular models of such chelates shows them to be severely strained. We do not favor such structures in this study, since the spectrum of the 2,6-(COOH)₂ product is found to undergo no substantial alteration when one of the carboxyl groups is blocked off by conversion to an ester or amide function.
 - (21) The present results also appear to rule out the possibility, once seriously considered,^{2a} that reduction of carboxyl-bound Co(III) in pyridinedicarboxylato complexes is initiated by attack at an uncoordinated COOH, COOMe, or CONH₂ group. If such a mechanism were important, the 2,5 complexes, in which the carboxyl groups are in conjugation with each other, would be expected to react much more rapidly than the 2,4, whereas the reverse is observed.
 - (22) It is assumed that proton transfers and substitutions at Cr(II) centers are very rapid in comparison to the other steps.
 - (23) It has been reported, for example (E. S. Gould, *J. Am. Chem. Soc.*, **92**, 6797 (1970)), that the rates at which 4-substituted benzoatopentaammine derivatives of (NH₃)₅Co^{III} are reduced by Cr²⁺ are very nearly independent of the net charge on the oxidant.
 - (24) See, for example, U. Bruhlmann and E. Hayon, *J. Am. Chem. Soc.*, **96**, 6169 (1974).
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Electron Transfer through Organic Structures. 38. Blocked Pyridinedicarboxylato Groups as Mediators in the Reactions of Copper(I) with Bound Cobalt(III)¹

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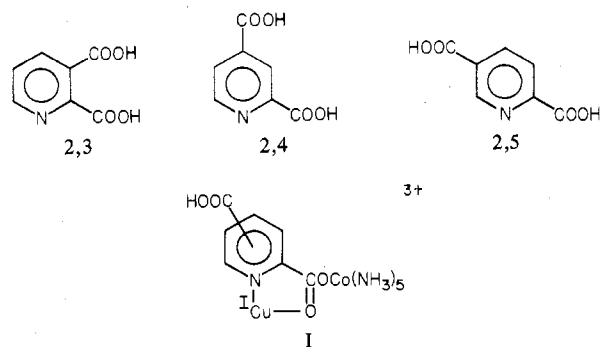
Pentaamminecobalt(III) derivatives of 2,3-, 2,4-, and 2,5-pyridinedicarboxylic acids, in which Co^{III} is attached specifically to the 2 position and, alternatively, to the position more distant from ring nitrogen, have been reduced with Cu⁺. Under comparable conditions, rates for the 2-COOC^{III} complexes are 10¹–10³ times those for the remotely coordinated complexes, with the latter reacting about as rapidly as ordinary straight-chain and aromatic carboxylato derivatives of (NH₃)₅Co^{III}. As with reductions by Cr²⁺, the greater rates for the 2-COOC^{III} oxidants are attributed to chelation in the Co^{III}–Cu^I precursor complexes. However, we find no evidence for operation of a radical-ion mechanism in reduction of the 4- and 5-COOC^{III} derivatives, a path which has been suggested to account for rate enhancements observed when these remotely coordinated oxidants react with the more strongly reducing Cr²⁺. The acidity patterns observed for the 2-COOC^{III} reductions are consistent with two mechanisms. In the first, a two-step path, a chelated precursor complex is formed (*k*₁) from the two metal centers with loss of H⁺, after which nonproductive dissociation of the precursor (*k*₋₁) competes with internal electron transfer (*k*₂). Values of *k*₁, which reflect substitution at two of the available positions at the Cu^I center, fall in the range 1–7 M⁻¹ s⁻¹, i.e., several powers of 10 less than rates for substitution of nonchelating ligands. The alternate mechanism, a three-step process, involves reversible deprotonation of the oxidant, formation of a chelated precursor (*k*₁'), and proton-induced internal electron transfer (*k*₂'). The latter mechanism leads to more credible values for the rate constants for substitution at Cu^I, but the proton-induced electron-transfer step is without precedent for systems of this sort. Choice between the two kinetically equivalent mechanisms is not yet possible.

In 1971 it was reported that the 2,3-, 2,4-, and 2,5-pyridinedicarboxylato derivatives of (NH₃)₅Co^{III} were reduced with Cu⁺ much more rapidly than were ordinary aliphatic and aromatic carboxylato complexes.² It was proposed at that time that cobalt(III) in these more rapid oxidants was coordinated at the 2-carboxyl, rather than at the position more remote from nitrogen, and that the high rates simply reflected the intervention of a chelated intermediate, I. Although the picture presented was internally consistent, it lacked certainty.

The recent availability³ of pyridinedicarboxylato derivatives, in which coordination by cobalt(III) is directed specifically by chemical blocking to the 2 or to the more remote position, has enabled us to examine the question more critically. The present results confirm, in a general way, earlier interpretations but, at the same time, disclose some new facets.

Experimental Section

Materials. Cobalt(III) complexes were available from a previous study³ or were prepared by published procedures.^{2,4} Lithium per-



chlorate and solutions of copper(I) perchlorate were prepared as described.²

Rate Measurements. Reactions were followed by measuring absorbance differences on a Cary spectrophotometer as described.^{2,5} Measurements were carried out under pseudo-first-order conditions