plexes of these metal species. The nitrile complexes of $(H_2O)_5Cr^{3+}$ can be expected to aquate much more rapidly than the $(NH_3)_5Co$ analogues, consistent with the observations here and previous work with 1,4-dicyanobenzene and fumaronitrile.[5,10]

Experimental Section

The chromium(II) solutions were prepared by zinc amalgam reductions of $Cr(OH_2)_6(ClO_4)_3$ stored under argon and handled by syringe techniques. General procedures, chemical sources, and analytical methods are described elsewhere.[6,10,12]

The reaction with iodoacetonitrile was done by adding aqueous Cr(II) to a deoxygenated solution of iodoacetonitrile so that initial reaction concentrations were 6.98×10^{-2} M Cr(II), 0.138 M $NCCH_2I$, and 0.50 M $HClO_4$ in a total volume of 20.0 mL. After 30 s, the solution was exposed to air and rapidly cooled in a dry ice–acetone slush. The solution was diluted to 60 mL with ice-cold water and charged onto a column of Dowex 50W-X2 (H^+ form) in a cold room at 5 °C. The unwanted products ($(H_2O)_5CrI^{2+}$, $(H_2O)_5CrCH_2CN^{2+}$) were eluted as quickly as possible with 0.20 M $HClO_4$–0.50 M $HClO_4$. Then, the desired product was eluted with 0.2 M $HClO_4$–1.0 M $NaClO_4$.[13] A portion of the eluent was transferred to a 10-cm path length cell to record the electronic spectrum and monitor the decomposition rate.

In the second preparative method a stock solution of 15 mL of 2.34 M $HClO_4$ and 15 mL of CH_3CN was prepared. To a 10-mL aliquot of this solution was added 0.14 g of $[(NH_3)_4CoCO_3]ClO_4$,[14] and the solution was sealed with a serum cap and deoxygenated with argon. Then, 1.0 mL of 0.49 M $Cr(ClO_4)_2$ solution was added and the reaction allowed to proceed for 2 min. Then, a 2.0-mL aliquot was taken and placed in a 10-cm path length cell containing appropriate amounts of $HClO_4$ and $LiClO_4$ solutions and water to give a final ionic strength of 1.0 M. To account for evaporation losses during degassing, a second 10-mL aliquot of the stock solution was treated in the same way except for the omission of reactants. Then, 2.0 mL of this solution was titrated with standard NaOH to determine the acidity, and the amounts of $HClO_4$ and $LiClO_4$ to be added to the spectrophotometer cell were calculated accordingly. For the temperature studies in 0.14 M H^+, the preparative solution contained 2 mL of CH_3CN in 9 mL of $HClO_4$–H_2O and a 2-mL aliquot of this was diluted to 13 mL with $HClO_4$–H_2O in a 5-cm path length cell.

Acknowledgment. The authors acknowledge financial support and fellowship support to W.C.K. from the Natural Sciences and Engineering Research Council of Canada.

Registry No. $(H_2O)_5CrNCCH_3^{3+}$, 89936-34-5.

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[12] Kupferschmidt, W. C.; Jordan, R. B. *Inorg. Chem.* **1981**, *20*, 3469.

[13] A small amount of a red product remained on the column. This product, which aquates to $Cr(OH_2)_6^{3+}$ and $(H_2O)_5CrCH_2CN^{2+}$, is tentatively identified as $(H_2O)_5CrNCCH_2Cr(OH_2)_5^{5+}$ and accounts for ~2% of the iodoacetonitrile.

[14] Since $[(NH_3)_4CoCO_3]ClO_4$ decarboxylates rapidly in acid, the actual oxidant is $(NH_3)_4Co(OH_2)_2^{3+}$. Problems were encountered at one stage because this reactant contained some nitrate salt impurity. It is recommended that the perchlorate is prepared by addition of aqueous $NaClO_4$ to a solution of $[(NH_3)_4CoCO_3]Cl$: Schlessinger, G. G. "Inorganic Laboratory Preparations"; Chemical Publishing Co., Inc.: New York, 1962.

Contribution from the Department of Chemistry,
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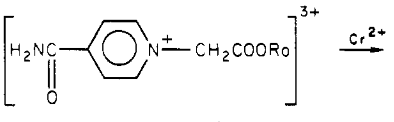
Electron Transfer. 68. Mediation by N-Substituted Isonicotinoyl Derivatives[1]

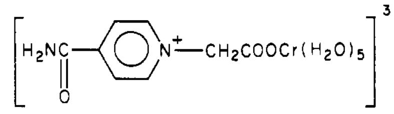
M. S. Ram, J. R. Barber, Jr., and E. S. Gould*

Received June 30, 1983

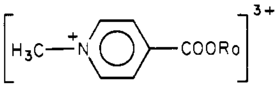
A report in 1979 described the reductions of such cobalt(III) complexes as the *N*-carboxymethyl derivative I, in which conjugation between $-COOCo^{III}$ and a pyridine ring activated by a γ-C(=O)NH– function was interrupted by a saturated unit.[2] It was found that reduction of I by Cr^{2+} proceeded about 700 times as rapidly as that of complex II, in which conjugation is unbroken. Since this acceleration did not persist when the $-CONH_2$ group was moved to the poorly activating β position (III), and since the primary oxidation product was found to be a $-COOCr^{III}$ complex (IV), it was proposed that the reduction of oxidant I proceeded through a doubly bridged intermediate of type V, in which the incoming chromium interacted with both the ring and the carboxyl function. Reductions, by Eu^{2+}, of both the cobalt complex I and its parent carboxylic acid exhibited similar enhancements. It was therefore suggested, at the same time, that an intermediate analogous to V might intervene in these reactions also.



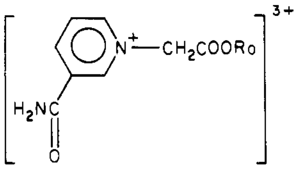
I, k_{Cr} = 660[3]



IV

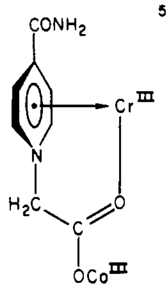


II, k_{Cr} = 0.93



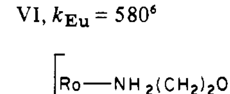
III, k_{Cr} = 0.059

Ro = "roseo" = $(NH_3)_5Co^{III}$



V

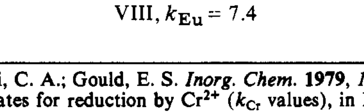
It was subsequently noted, however, that rapid Eu^{2+} reduction of the ligand did not require the *N*-carboxymethyl function,[4] i.e., that marked enhancement remained when the latter unit was replaced by a number of strongly electron-attracting N-bound aryl groups (e.g., VI). Moreover, it was



VI, k_{Eu} = 580[6]

$[Ro-NH_2(CH_2)_2OH]^{3+}$

VII, k_{Eu} = 0.0085



VIII, k_{Eu} = 7.4

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[1] Support of this work by the National Science Foundation (Grant No. 8022881) is gratefully acknowledged.

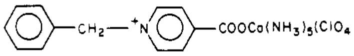
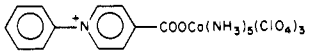
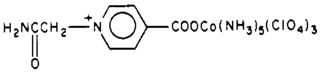
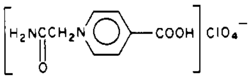
[2] Radlowski, C. A.; Gould, E. S. *Inorg. Chem.* **1979**, *18*, 1289.

[3] Specific rates for reduction by Cr^{2+} (k_{Cr} values), in M^{-1} s^{-1}, refer to reactions at 25 °C (μ = 1.0).

[4] Ram, M. S.; Gould, E. S. *Inorg. Chem.* **1983**, *22*, 2454.

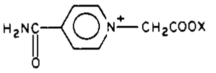
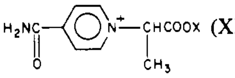
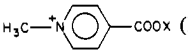
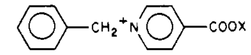
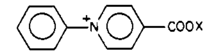
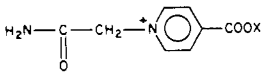
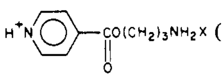
0020-1669/84/1323-1988$01.50/0

Table I. Analyses of Pentaamminecobalt(III) Complexes of *N*-Substituted Isonicotinic Acids

	% C		% H		% N	
	calcd	found	calcd	found	calcd	found
 (X)	23.8	23.8	4.10	3.95		
 (XI)	22.4	22.3	3.62	3.74		
 (XII)	15.4	15.5	3.69	3.75	15.73	15.67
 (IX)[a]	34.2	34.2	3.20	3.09	9.96	9.92

[a] Parent ligand not previously prepared.

Table II. Specific Rates for Reduction of Isonicotinoyl Derivatives[a]

	k_{Cr}[b] X = Co^{III}	k_{Eu}[c] X = H	k_{Cr}/k_{Eu}	k_{Eu}[d] X = Co^{III}
 (I)	6.6×10^2 [e]	170[e]	3.9	160[e]
 (XIII)	5.5×10^2 [e]	90[e]	6.1	95[e]
 (II)	0.93[f]	15[g]	0.062	2.4[h]
 (X)	1.60	73	0.022	
 (XI)	6.2	5.8×10^2 [i]	0.010	
 (XII)	5.7	3.8×10^2	0.015	
 (XIV)	0.0088[j]	4.4[j]	0.002	3.7[j]

[a] In M^{-1} s^{-1} at 25 °C. [b] Specific rates for reduction of Co(III); $\mu = 0.20$ unless otherwise indicated. [c] Specific rate for the 1e reduction of the free ligand to its radical, using Eu^{2+}; obtained from catalytic studies,[4,10] reaction medium 1.0 M $HClO_4$. [d] Specific rate for reduction of Co(III); $\mu = 1.0$. [e] Reference 2, $\mu = 1.2$. [f] $\mu = 1.0$. [g] Reference 10. [h] Srinivasan, V. S.; Hu, Y.-R.; Gould, E. S. *Inorg. Chem.* 1980, *19*, 3470. [i] Value for reduction of the methyl ester. [j] $\mu = 1.0$.[5]

reported[5] that complex VIII is reduced by Eu^{2+} about 10^3 times as rapidly as its unacylated analogue, VII, thus indicating that the carboxyl group is not essential for isonicotinoyl-derived k_{Eu} increases in this interrupted system.

Since the evidential base for intermediates of type V appears to be narrowing, one may ask whether the suggested intervention of such a structure is truly necessary to account for the kinetic patterns exhibited by Cr^{2+} reductions or whether, as with Eu(II), comparable enhancements may occur in instances where such a structure cannot form. We here describe additional experiments bearing on this question.

Experimental Section

Materials. Solutions of $Cr(ClO_4)_2$[7] and $Eu(ClO_4)_2$[8] were prepared as described. *N*-Benzylisonicotinic acid was available from an earlier study.[4] The analogous *N*-phenyl acid was prepared through hydrolysis of its methyl ester[4] by treatment with 1 M $HClO_4$ at 90 °C for 15 h.

The *N*-carbamoylmethyl derivative of isonicotinic acid (IX) was prepared by treating a solution of sodium isonicotinate with a 25% excess of iodoacetamide at 90 °C for 4 h. The mixture was cooled and then passed through an anion-exchange column (Bio-Rad AG 2-X8) in its HCO_3^- form. The solution was evaporated to dryness in vacuo, the residue was dissolved in a minimum volume of water, and the desired acid precipitated as its perchlorate by addition of $HClO_4$.

Cobalt(III) complexes were prepared from the parent acids and aquopentaamminecobalt(III) perchlorate as described.[7] The complex from the *N*-carbamoylmethyl-substituted acid (XII) precipitated in impure state from the reaction mixture but could be purified by separation on Bio-Gel P-2, followed by recrystallization from 0.01 M $HClO_4$. Elemental analyses of new complexes and of the *N*-carbamoylmethyl ligand are given in Table I. None of these perchlorates presented significant problems in handling.

Kinetic Measurements. Rates for reduction of Co(III) complexes were estimated from measurements of absorbance decreases on the Cary 14 spectrophotometer as described.[7,8] Measurements were made at 502 nm. Reactions were first order each in Co(III) and Cr(II) but were run with at least a 10-fold excess of reductant with $[Co^{III}] = 0.0004–0.002$ M and $[Cr^{2+}] = 0.004–0.05$ M. Reactions were generally carried out in 0.20 M $HClO_4$ and were followed for at least 4 half-lives. Kinetic curves were nearly exponential, but significant decreases in apparent half-life periods were generally observed as the reactions proceeded. Such departures from pseudo-first-order behavior arise from catalysis of the reaction by the Cr(III) product formed, an effect that can be made much more pronounced at lower acidities.[9]

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(5) Goli, U. B.; Gould, E. S. *Inorg. Chem.* **1984**, *23*, 221.

(6) Specific rates for reduction by Eu^{2+} (k_{Eu} values), in M^{-1} s^{-1}, refer to reactions at 25 °C ($\mu = 1.1$). The value for 1e reduction of ligand VI was obtained from studies of catalysis, by VI, of the Eu(II) reduction of $Co(NH_3)_5(py)^{3+}$.[4]

(7) Gould, E. S.; Taube, H. *J. Am. Chem. Soc.* **1964**, *86*, 1318.

(8) (a) Dockal, E. R.; Gould, E. S. *J. Am. Chem. Soc.* **1972**, *94*, 6673. (b) Fan, F.-R. F.; Gould, E. S. *Inorg. Chem.* **1974**, *13*, 2639.

Rate constants for the primary reactions were obtained by extrapolation to zero time. Agreement between extrapolated values derived from replicate runs was within 10%. Temperatures were kept at 25.0 ± 0.2 °C during the entire series of experiments.

The specific rate for Eu(II) reduction of ligand IX to its radical was estimated by using this ligand as a catalyst in the Eu(II) reduction of excess $\mathrm{Co(NH_3)_5(py)^{3+}}$. Under the conditions used, reduction of the ligand, which is the rate-determining step in the catalytic sequence,[10] is monitored by following the disappearance of Co(III) at 475 nm. As in earlier work,[10] k_{Eu} values obtained from replicate runs agreed to better than 8%.

Results and Discussion

Specific rates of $\mathrm{Cr^{2+}}$ reduction of Co(III) complexes of N-substituted ligands appear in Table II. These are compared with rate constants for the 1e reduction of the free ligands to their radicals (obtained from past catalytic studies)[4,10] and with values for $\mathrm{Eu^{2+}}$ reductions of the complexes. Where the latter are available, they are seen to lie remarkably near k_{Eu}'s for the ligands, reminding us that the rate-determining steps for the two classes of $\mathrm{Eu^{2+}}$ reduction are closely related, i.e., that reductions of these Co(III) complexes are initiated by acceptance of an electron by the isonicotinoyl ring system (the chemical mechanism).[5] In the absence of accelerating groups, this transfer is seen to proceed with a specific rate in the range 2–15 $\mathrm{M^{-1}\,s^{-1}}$ (25 °C, $\mu = 1.0$). In a single instance (ligand II), the Co(III) complex is found to be reduced significantly more slowly than the parent ligand; here $\mathrm{Co^{III}}$ is positioned unusually close to the ring, and electrostatic repulsion between metal centers may be playing a part.

By affixing strongly electron-attracting substituents to the ring nitrogen, k_{Eu} may be made to approach 10^3. Units that function in this manner are *N*-carboxymethyl (I), *N*-aryl (XI),[11,12] and *N*-carbamoylmethyl (XII). It has been shown[13] that replacement of a γ-$\mathrm{CONH_2}$ group (as in I) by a γ-$\mathrm{COOCH_3}$ group (as in XI) results in only a 3-fold increase in k_{Eu}. Since ligand XI is here likewise found to be reduced just 3 times as rapidly as ligand I, we may infer that no special advantage results from incorporation of a carboxyl (rather than a phenyl) into the N-bound group.

Rate-enhancing effects for $\mathrm{Cr^{2+}}$ reductions are seen, however, to be considerably more specific. In the absence of a carboxyl group (oxidant XIV), k_{Cr} values drop close to the range characteristic of outer-sphere reductions of $\mathrm{(NH_3)_5Co^{III}}$ derivatives of N-donor ligands (10^{-4}–10^{-3} $\mathrm{M^{-1}\,s^{-1}}$).[8a] Moreover, only modest increases (in comparison to those for the *N*-methyl complex, II) result from attachment of those *N*-bound substituents that are most effective for $\mathrm{Eu^{2+}}$. The $\mathrm{^+NCH_2CONH_2}$ group (complex XII), which is closely related structurally to $\mathrm{^+NCH_2COOH}$ (complex I), exhibits only a marginal effect with Co(III) absent from the side chain. The most rapid oxidants, by far, are those that feature the ring-bound $\mathrm{^+NCHCOOCo^{III}}$ unit (I and XIII). Only from these may the doubly bridged precursor, V, be assembled. The latter structure then remains a reasonable intermediate for rapid reductions by $\mathrm{Cr^{2+}}$, although it can no longer be taken to be essential for those by $\mathrm{Eu^{2+}}$.

The difference in structural requirements may be considered in conjunction with differences in attenuation patterns associated with the two reductants. It has been reported[14] that k_{Cr} values in homologues of complex I and related oxidants fall off very sharply as the chain between the pyridine ring and $\mathrm{-COOCo^{III}}$ is lenghened by interposition of additional carbon atoms, whereas k_{Eu} values decline much more gradually. Moreover, in some carboxyl-free systems marked isonicotinoyl-related enhancements of k_{Eu} (but not k_{Cr}) may persist even though the activated ring is separated from the $\mathrm{Co^{III}}$ center by as many as seven atoms.[5] It has been proposed[14] that the different symmetry character of the donor orbitals for these two reducing centers is reflected in differences in their mode of action, i.e., that transmission of spin density between the activated ring and $\mathrm{Co^{III}}$ operates mainly through the intervening bonds in Cr(II) systems but principally through space in Eu(II) systems. The present findings appear to be consistent with this suggestion.[15,16]

Registry No. II, 74911-56-1; IX, 90219-69-5; X, 90219-63-9; XI, 90219-65-1; XII, 90219-67-3; XIV, 90219-70-8; Cr, 7440-47-3; Eu, 7440-53-1.

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(9) Barber, J. R., Jr.; Gould, E. S. *J. Am. Chem. Soc.* **1971**, *93*, 4045.

(10) See, for example: Fanchiang, Y.-T.; Carlson, R. R.; Thamburaj, P. K.; Gould, E. S. *J. Am. Chem. Soc.* **1977**, *99*, 1973. The catalytic sequence is

$$\mathrm{Lig} \underset{\mathrm{Eu^{3+}},\ k_{-1}}{\overset{\mathrm{Eu^{2+}},\ k_1}{\rightleftharpoons}} \mathrm{Lig}\cdot \xrightarrow[k_2]{\mathrm{Co^{III}}} \mathrm{Lig} + \mathrm{Co^{2+}}$$

The ratio k_2/k_{-1} (but not individual values for each) may be obtained from experiments with Eu(II) in excess and in the presence of Eu(III).[4] This ratio, for ligand IX, is 18 (25 °C, 1.0 M $\mathrm{HClO_4}$).

(11) The largest k_{Eu} value for an isonicotinoyl derivative is 1.1×10^3 $\mathrm{M^{-1}\,s^{-1}}$, reported for the *N*-(2-naphthyl) derivative of methyl isonicotinate.[4] Still larger values result from incorporation of a second, but not a third, carboxyl group in the ring.[12]

(12) See, for example: Fanchiang, Y.-T.; Heh, J. C.-K.; Gould, E. S. *Inorg. Chem.* **1978**, *17*, 1142.

(13) Radlowski, C. A.; Chum, P.-W.; Hua, L.; Heh, J.; Gould, E. S. *Inorg. Chem.* **1980**, *19*, 401. Values of k_{Eu} reported by these workers are 2.0 $\mathrm{M^{-1}\,s^{-1}}$ for isonicotinamide and 6.2 $\mathrm{M^{-1}\,s^{-1}}$ for ethyl isonicotinate (25 °C, 1.0 M $\mathrm{HClO_4}$).

(14) Srinivasan, V. S.; Radlowski, C. A.; Gould, E. S. *Inorg. Chem.* **1981**, *20*, 2094.

(15) A reviewer has asked how certain we are that the Cr(II) reductions of the (carboxylato)cobalt(III) complexes in this study proceed by the inner-sphere route. Although we have characterized the Cr(III) product only from oxidant I, we cite the study by Fan,[16] who has estimated outer-sphere contributions to reactions of this type as 10^{-5}–10^{-2} times the observed rates. Reduction of complex XIV, in which the carboxyl cannot assume a lead-in function toward Co(III), would be expected to be outer sphere.

(16) Fan, F.-R. F.; Gould, E. S. *Inorg. Chem.* **1974**, *13*, 2647.

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Howard University, Washington, D.C. 20059

Magnitudes of Ionic Strength Effects in Porphyrin Metalation and Acid Solvolysis Reactions

Jonas Nwaeme and Peter Hambright*

Received April 26, 1983

In metalation and acid-catalyzed solvolysis reactions of porphyrins and metalloporphyrins, certain peripherally positively charged porphyrins have been reported to have anion terms in their rate laws, while other positive and negative derivatives lack such features. The following analysis indicates that anion catalysis is partially (but not exclusively) attributable to ionic strength effects.

For a number of positively charged water-soluble porphyrins ($\mathrm{H_2}$–P) such as tetrakis(*N*-methyl-4-pyridyl)porphyrin[1] and its 3- and 2-pyridyl analogues[2] studied in nitrate media, the kinetics of divalent metal ion incorporation show rate = $k_f[\mathrm{H_2{-}P}][\mathrm{M^{2+}}][\mathrm{NO_3^-}]$. The rate law for the solvolysis of the corresponding zinc porphyrins[3] at high acidities in $\mathrm{HNO_3}$ is rate = $k_{\mathrm{D}}[\mathrm{Zn{-}P}][\mathrm{H^+}]^2[\mathrm{NO_3^-}]$. The unusual first-order term in nitrate was suggested by the fact that plots of the observed specific rates ($k_{\mathrm{obsd}}/[\mathrm{M^{2+}}]$ or $k_{\mathrm{obsd}}/[\mathrm{H^+}]^2$) vs. $[\mathrm{NO_3^-}]$ were

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(1) Hambright, P.; Chock, P. *J. Am. Chem. Soc.* **1974**, *96*, 3123.

(2) Reid, J.; Hambright, P. *Inorg. Chem.* **1977**, *16*, 968.

(3) Shah, B.; Hambright, P. *J. Inorg. Nucl. Chem.* **1970**, *32*, 3240.

0020-1669/84/1323-1990$01.50/0