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Electron Transfer. 55. Reductions of Pyridinecarboxylato-Bridged Dicobalt(III) Complexes[1]

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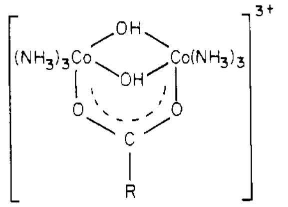
The reactions of seven new carboxylato-bridged dicobalt(III) complexes, analogous to dimer I, with several metal-centered reducing agents have been examined. Three of the oxidants are pyridinedicarboxylato derivatives in which the 2-carboxyl links two Co(III) centers and the second carboxyl has been converted to a $-CONH_2$ group. The other dimers feature an activated pyridine ring separated from the bridging carboxyl by a saturated fragment. Specific rates in each case are taken to be determined by the reduction of the first of the two Co(III) centers. The 2,4- and 2,5-pyridinedicarboxylato-bridged oxidants, III and IV, are reduced by V^{2+}, Eu^{2+}, Cr^{2+}, and U^{3+} from 10^2 to 10^7 times as rapidly as the analogous benzoato-bridged oxidant, but accelerations with $Ru(NH_3)_6^{2+}$ are slight. These rapid reductions exhibit rates independent of acidity in the range 0.2–1.0 M H^+, indicating that initial attack has occurred at the amide function, rather than the hetero nitrogen. The slower reductions of the 2,3-isomer (complex II) by Cr^{2+} and V^{2+} (but not by Eu^{2+}) appear to proceed in part by attack at the ring. Although the parent ligands are of the type favoring electron transfer via a ligand-centered radical-cation intermediate, yields of Co^{2+} are quantitative, demonstrating that such an intermediate, if formed, is not perceptibly diverted by dimerization or disproportionation, in contrast to the analogous intermediates interceding in very rapid reductions of oxidants with α-keto carboxylato bridges. Of the oxidants featuring "interrupted" conjugation, dimer V (derived from $Inic^+CH_2COOH$), but not its 3-substituted isomer, VI (derived from Nic^+CH_2COOH), is reduced unusually rapidly by Cr^{2+}, Eu^{2+}, and U^{3+}. The structure of V virtually dictates a radical-cation mechanism, and here again there is no significant diversion of the intermediate. For Cr^{2+} reductions, interaction between the activated pyridine ring and the Co(III) center falls off sharply as the insulating fragment is lengthened from one to three atoms, but this attenuation appears to be much less sudden for Eu^{2+} reductions, suggesting that through-bond interaction predominates with the first of these reductants with through-space transmission becoming more important with the second.

Although early reports concerning the inner-sphere reductions of carboxylato-bound cobalt(III) emphasized the effectiveness of suitably substituted pyridinecarboxylato and -dicarboxylato ligands as redox mediators,[3] ambiguities persisted as to the mode of action of such groups. When, for example, incorporation of such substitutents was found to result in marked increases in rates of reduction by Cr^{2+} and Cu^+ (in cases where the bound carboxyl and the ring nitrogen lay in conjugation), it was initially supposed[3ac] that the principal reaction path involved attack by the reductant at the hetero nitrogen and transmission of the reducing electron through the pyridine ring, a path which was indeed subsequently demonstrated in related systems.[4] More recently, however, evidence has accumulated[5] supporting the conclusion that monomeric pyridinecarboxylato complexes of cobalt(III) (irrespective of detailed structure and reaction rate) are reduced by Cr^{2+}, V^{2+}, and Eu^{2+} predominantly via initial attack on the ligated carboxyl and that electron transfer via the ring nitrogen plays at most a minor part.

Electron-transfer studies using (μ-carboxylato)dicobalt(III) complexes of type I have been instructive.[6] In such oxidants, the carboxyl group has been "blocked off" by ligation to the second Co^{III}, leaving only a very slow[7] outer-sphere path and, where available, a "remote" path through the ring nitrogen. Thus, it has been found[6a] that the 2- and 4-py isomers (but not the poorly conjugated 3-py isomer) of dimeric complex I are reduced by Cr^{2+} (at 25 °C, 0.05 M H^+) 200–300 times as rapidly as the corresponding μ-benzoato dimer[7] and that reductions of the pyridinecarboxylato-bridged dimers are retarded by protonation, strongly suggesting, once again, remote attack in these cases.



I (R = 2-, 3-, 4-py)

In the present work, we have examined reductions of additional complexes of type I (some of them strikingly accelerated) derived from 2,3-, 2,4-, and 2,5-pyridinedicarboxylic acids. So that preparative complications and ambiguities in interpretation of kinetic results could be minimized, the carboxyl more distant from the ring nitrogen has been selectively tied off by conversion to an amide group,[5b] leaving only the 2-COOH available for bridging. Besides including studies dealing with several additional reductants, we also report experiments concerned with the action of certain pyridine-derived ligands featuring interrupted conjugation, a type which has recently been of particular interest to us.[8]

Experimental Section

Materials. Lithium perchlorate[3c] and solutions of $Eu(ClO_4)_2$,[9] $V(ClO_4)_2$,[10] $Cr(ClO_4)_2$,[3a] $Ru(NH_3)_6Cl_2$,[11] and $U(ClO_4)_3$[12] were

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(2) (a) On leave from Vivekananda College, Mylapore, Madras, India. (b) Kent State University.

(3) See, for example: (a) Gould, E. S.; Taube, H. *J. Am. Chem. Soc.* **1964**, *86*, 1318. (b) Gould, E. S. *Ibid.* **1965**, *87*, 4730. (c) Dockal, E. R.; Everhart, E. T.; Gould, E. S. *Ibid.* **1971**, *93*, 5661.

(4) See, for example: (a) Nordmeyer, F.; Taube, H. *J. Am. Chem. Soc.* **1968**, *90*, 1162. (b) Jwo, J.-J.; Haim, A. *Ibid.* **1976**, *98*, 1172.

(5) (a) Thamburaj, P. K.; Loar, M. K.; Gould, E. S. *Inorg. Chem.* **1977**, *16*, 1946. (b) Heh, J. C.-K.; Gould, E. S. *Ibid.* **1978**, *17*, 3138.

(6) (a) Spiecker, H.; Wieghardt, K. *Inorg. Chem.* **1976**, *15*, 909. For related earlier studies, see: (b) Scott, K. L.; Wieghardt, K.; Sykes, A. G. *Ibid.* **1973**, *12*, 655. (c) Hyde, M. R.; Wieghardt, K.; Sykes, A. G. *J. Chem. Soc., Dalton Trans.* **1976**, 690.

(7) Wieghardt, K.; Sykes, A. G. *J. Chem. Soc., Dalton Trans.* **1974**, 651.

(8) (a) Radlowski, C. A.; Gould, E. S. *Inorg. Chem.* **1979**, *18*, 1289 (b) Srinivasan, V. S.; Radlowski, C. A.; Gould, E. S. *Ibid.* **1981**, *20*, 2094, 3172.

(9) (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.

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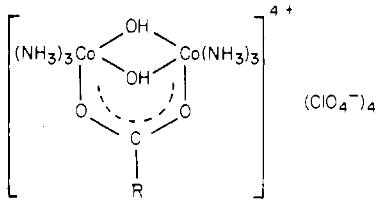
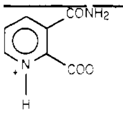
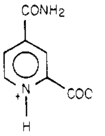
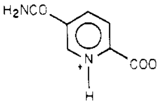
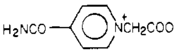
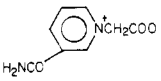
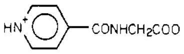
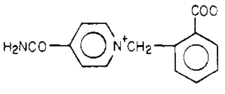
Table I. (μ-Carboxylato)bis(μ-hydroxo)bis[triamminecobalt(III)] Perchlorates



RCOO	% C calcd	% C found	% H calcd	% H found	% Co calcd	% Co found[a]	λ_{max}, nm	ϵ_1	λ_{max}, nm	ϵ_2
 (II, pK_A = 1.27[c])	10.24	10.31	3.17	3.35	14.4	13.5	373[b]	239	525	106
 (III, pK_A = 1.33[c])	10.24	10.36	3.17	3.20	14.4	13.5	362[b]	286	524	112
 (IV, pK_A = 1.06[c])	10.24	10.49	3.17	3.23	14.4	13.9	365[b]	261	525	108
 (V)	11.51	11.57	3.36	3.46	14.2	13.8	372[b]	274	525	110
 (VI)	11.51	10.81	3.36	3.54	14.2	13.6	362[b]	273	524	109
 (VII)	11.51	10.75	3.36	3.58	14.2	13.5	364[b]	254	524	108
 (VIII)	18.46	18.47	3.52	3.78	13.0	12.2				

[a] See ref 3a. [b] Shoulder. [c] 25 °C, 1 M ClO_4^-.

prepared as described. Half-amides of pyridinedicarboxylic acids, each of which featured a free 2-COOH group, were prepared by the method of Thunus and Dejardin-Duchens.[5b,13] Ligands having interrupted conjugation, used in preparation of dimeric oxidants V–VIII, were available from previous studies.[8] Preparation of the tris(μ-hydroxo) complex $(NH_3)_3Co(OH)_3Co(NH_3)_3{}^{3+}(ClO_4^-)_3$ and conversions to carboxylato-bridged dimeric cobalt(III) complexes of type I have been described.[14] Analyses of dimeric complexes appear in Table I.

Rate Measurements. Rates were estimated from absorbance changes on the Beckman Model 5260 recording spectrophotometer of the Durrum-Gibson stopped-flow spectrophotometer as described.[3ab,15] Reductions were monitored at 524 nm. Reactions were first order in oxidant and reductant but were generally carried out under pseudo-first order conditions using at least a tenfold excess of reductant. A number of the reductions with Cr^{2+}, V^{2+}, and Eu^{2+} were run at several known concentrations of $HClO_4$, while total ionic strength was kept near unity by addition of $LiClO_4$. Reactions of U^{3+} were carried out in 0.2 M $HClO_4$, whereas those of $Ru(NH_3)_6{}^{2+}$ were carried out (under argon) in 0.5 M LiCl in the presence of 0.01 M HCl. Reactions were generally followed for at least 5 half-lives. Rate constants evaluated from successive half-life values in a single run agreed to within 6%, and specific rates obtained for replicate runs on the Beckman spectrophotometer checked to better than 8%. Successive oxidations on the Durrum (with the same pair of master solutions) were repeated until kinetic curves for three consecutive runs were superimposible. Specific rates obtained by stopped flow from different master solutions agreed to better than 6%. A number of reductions by Eu^{2+} and V^{2+} yielded, instead of the usual logarithmic curves, decay curves that were much more nearly linear, indicating autocatalysis of the type reported in previous studies.[8,9] In such cases the autocatalytic component was suppressed, either totally or partially, by addition of excess Eu^{3+} or V^{3+} as described,[8a,16] allowing specific rates pertaining to the uncatalyzed reaction to be estimated. Aside from the very rapid reductions, which were monitored at 20 °C, temperatures were kept at 25.0 ± 0.2 °C during this series of experiments.

Stoichiometry Studies. Stoichiometry experiments, in which cobalt(III) and a ligand bound to it were made to compete for a deficient quantity of reductant, were carried out as described.[3a,14,17] The procedure was standardized by using the Cr^{2+} reduction of the monomeric $(NH_3)_5Co^{III}$ derivative of maleic acid.[18] Results are presented in Table II. For slow reactions, mixtures were allowed to stand for several hours before analyzing for Co^{2+}; in such cases, the results represent lower limits since the reductant was very probably consumed, in part, by traces of O_2 diffusing into the vessel.

pK_A Determinations. pK_A values for the three cobalt(III) derivatives of pyridinedicarboxylic acid (II, III, IV) were estimated by measuring the absorbance of these complexes in the region 270–276 nm in various solutions of known pH (25 °C, 1 M ClO_4^-). Because differences were small (less than 25% of the total absorbance), the uncertainties in the resulting pK_A's (Table I) are relatively great (0.05 unit).

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(10) (a) Guenther, P. R.; Linck, R. G. *J. Am. Chem. Soc.* **1969**, *91*, 3769. (b) Linck, R. G. *Inorg. Chem.* **1970**, *9*, 2529.

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

(12) Loar, M. K.; Sens, M. A.; Loar, G. W.; Gould, E. S. *Inorg. Chem.* **1978**, *17*, 330.

(13) Thunus, L.; Dejardin-Duchene, M. *J. Pharm. Belg.* **1969**, *24*, 3.

(14) Srinivasan, V. S.; Singh, A. N.; Wieghardt, K.; Rajasekar, N.; Gould, E. S. *Inorg. Chem.* **1982**, *21*, 2531.

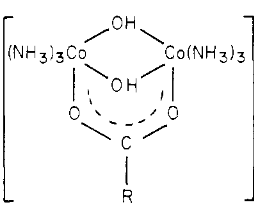
(15) Gould, E. S. *J. Am. Chem. Soc.* **1974**, *96*, 2373.

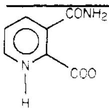
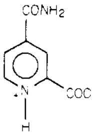
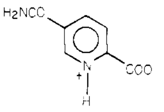
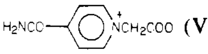
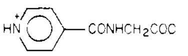
(16) Srinivasan, V. S.; Hu, Y.-R.; Gould, E. S. *Inorg. Chem.* **1980**, *19*, 3470.

(17) Gould, E. S.; Johnson, N. A.; Morland, R. B. *Inorg. Chem.* **1976**, *15*, 1929.

(18) Olson, M. V.; Taube, H. *Inorg. Chem.* **1970**, *9*, 2072.

Table II. Yields of Co^{2+} from Action of Metal-Center Reductants on Dicobalt(III) Complexes[a]

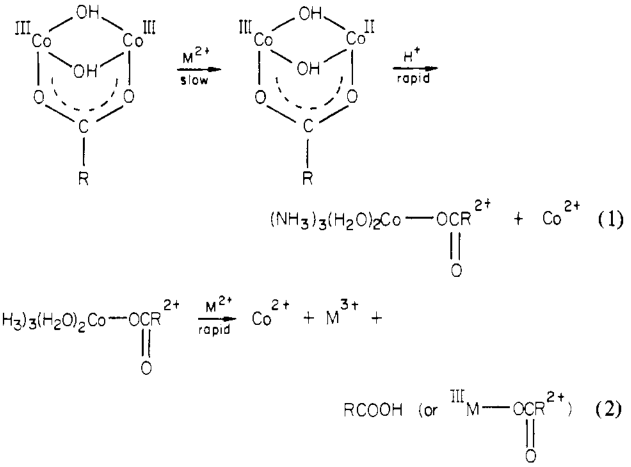


RCOO	yield of Co^{2+}, %				
	V^{2+}	Cr^{2+}	Eu^{2+}	Ru^{II} [b]	U^{3+}
 (II)	100	59	100	100	98
 (III)	100	98	94	100	98
 (IV)	102	94	103	101	
 (V)		96	100		
 (VII)			70		92

[a] $[H^+] = 1.0$ M, unless otherwise indicated; [oxidant] = 0.0050 M; [reductant] = 0.0020 M; reductant was added to Co(III).
[b] Reductions by $Ru(NH_3)_6{}^{2+}$ were carried out in a solution 0.5 M in LiCl and 0.01 M in HCl.

Results and Discussion

Sequence (1)–(2) represents the reductions of the dimeric



(1)

(2)

complexes in the present study. Arguments developed earlier[14] that the initial act of electron transfer is much slower than either of the subsequent steps and that kinetic studies of this type therefore measure the specific rates of reduction of the dimers (rather than the monomeric intermediates) are taken to apply to the series at hand.

Kinetic data appear in Table III,[19] in which are also included, for comparison, specific rates pertaining to two bridged dimers devoid of the pyridine ring, the structures of which dictate initial reduction solely via an outer-sphere path. Note that all oxidants except complex II are reduced with rates independent of acidity in the range 0.20–1.0 M H^+.[20]

The most remarkable values are undoubtedly those for the 2,4- and 2,5-pyridinedicarboxylato-bridged oxidants, III and IV. Comparing these with rates for reduction of the μ-benzoato dimer,[7,14] we find acceleration factors of 10^6–10^7 for Cr^{2+}, 10^3–10^4 for Eu^{2+}, 10^2 for V^{2+}, and 10^5 for U^{3+}.[21] Since less than tenfold accelerations are observed for $Ru(NH_3)_6{}^{2+}$, which must react without bridging, it is very probable that the rapid reactions with the other metal center reductants are, in very large part, inner sphere, necessarily utilizing a remote path.

Two lines of evidence, however, weigh against a mechanism featuring attack by the reductant at the pyridine nitrogen (a route suggested for reactions of the conjugated mono(carboxylato) analogues[6a]). Since the oxidants exist mainly in their ring-protonated forms in the systems at hand, predominant attack at the hetero nitrogen would be reflected in an inverse-acid rate law, contrary to what is observed. Moreover, rate enhancement is seen to extend, although less dramatically, to reductions by Eu^{2+}, a reducing center which, in the past,[5a,9a] has exhibited great reluctance to utilize the pyridine nitrogen in a "lead-in" capacity.[22,23]

We thus conclude that the very rapid reductions of the 2,4- and 2,5-substituted dimers in this series occur by attack at the amide function, a unit which has shown to be an effective lead-in group for reductions by Cr(II)[4a] and Eu(II).[24,25] Note that the $-CONH_2$ group in the 2,4-dimer lies in conjugation with the ring nitrogen, whereas that in the 2,5-dimer is conjugated with the bridging carboxyl.

Rate enhancements in reduction of the 2,3-dimer (II), although perceptible, are very much less striking, suggesting that steric interference between the adjacent ring substitutents keeps one or both of them out of the plane of the ring, greatly diminishing conjugative interaction. In addition, the Cr^{2+} and V^{2+} reductions of this complex conform to rate expressions featuring prominent inverse-acid components. The data on hand for these reductions, spanning the relatively narrow range 0.2–1.0 M H^+, are consistent with a k_{Cr} of $(0.030 + 0.052[H^+]^{-1})$ M^{-1} s^{-1} and a k_V of $(0.61 + 0.11[H^+]^{-1})$ M^{-1} s^{-1}. The inverse-acid terms pertain to the deprotonated form of the oxidant, the hetero nitrogen of which is available as a lead-in site. Hence this oxidant, alone in the present series, appears to react, in substantial part, via attack at the ring, a path for which there is strong evidence in the case of the analogous 2- and 4-mono(carboxylato)-bridged oxidants.[6a] Division of the rate constants for the inverse-acid components by K_a for this oxidant (6.8×10^{-2} M^{-1} in 1.0 M $LiClO_4$) yields the bimolecular specific rates 0.76 and 1.6 M^{-1} s^{-1} for Cr^{2+} and V^{2+}

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(19) The rate constants given refer to the disappearance of the dimeric species, rather than to the formation of Co^{2+}. Values for the latter process would be twice those entered.

(20) A slight acid-dependent component has been reported for Cr^{2+} reduction of the μ-benzoato dimer,[7] but this is presumably associated with slow cleavage of the bridge and is unrelated to the processes of interest here.

(21) Note that the k_U values for the more rapid oxidants (Table III) are quite similar and appear to approach 3×10^6 M^{-1} s^{-1}, suggesting that these specific rates are approaching a limit imposed by substitution at the U(III) center.

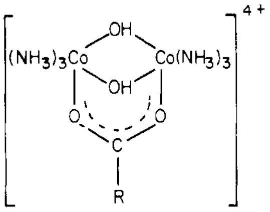
(22) A related point pertains to the observed rates for V^{2+} reduction of dimers III and IV. If initial attack were to occur mainly at the ring nitrogen, the specific rates for reaction of the deprotonated oxidants, estimated by dividing the rate constants at $[H^+] = 1.0$ by K_A's of the dimers (Table I), would approach 100 M^{-1} s^{-1}, well in excess of the accepted substitution-controlled upper limit (40 M^{-1} s^{-1})[23] for inner-sphere V(II) reductions of positively charged oxidants.

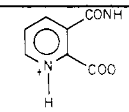
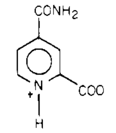
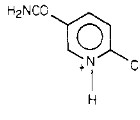
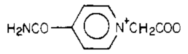
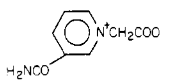
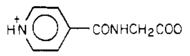
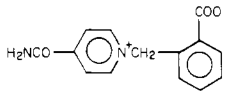
(23) See, for example: Baker, B. R.; Orhanovic, M.; Sutin, N. *J. Am. Chem. Soc.* **1967**, *89*, 722.

(24) Fanchiang, Y.-T.; Heh, J. C.-K.; Gould, E. S. *Inorg. Chem.* **1978**, *17*, 1142.

(25) Fanchiang, T.-T.; Carlson, R. R.; Thamburaj, P. K.; Gould, E. S. *J. Am. Chem. Soc.* **1977**, *99*, 1073.

Table III. Specific Rates for Reductions of Bridged Dimeric Cobalt(III) Complexes[a]



RCOO	$k_{\mathrm{Cr(II)}}$	$k_{\mathrm{Eu(II)}}$	$k_{\mathrm{V(II)}}$	$k_{\mathrm{Ru(II)}}$[b]	$k_{\mathrm{U(III)}}$[c]
 (II)	0.087 0.127[e] 0.29[f]	0.58[d,i] 0.34[d,j]	0.69 0.87[e] 1.14[f]	1.10	7.4×10^4
 (III)	1.17×10^4 [h] 1.16×10^4 [e,h] 0.97×10^4 [f,h]	5.3×10^2 [d,h]	9.9[d]	0.63	2.5×10^6
 (IV)	1.16×10^3 [h] 1.17×10^3 [e,h] 0.84×10^3 [f,h]	1.7×10^2 [d,h]	8.5	0.35	2.5×10^6
 (V)	16.8	86[d]	1.82	0.94	2.5×10^6
 (VI)	0.043	0.103	0.175	0.60	8.0×10^3
 (VII)	0.014	0.20	0.086	0.47	6.2×10^2
 (VIII)	0.0060	13.1[d]	0.138[d]	1.01	
acetato[g]	0.0014	0.0086	0.053	0.062	1.26
benzoato[g]	0.0017	0.0102	0.067	0.117	2.8

[a] Specific rates in M^{-1} s^{-1} at 25 °C (1 M $HClO_4$) unless otherwise indicated. [b] Reductions with $Ru(NH_3)_6{}^{2+}$ were carried out in 0.5 M LiCl; $[H^+] = 0.01$ M. [c] Reactions were carried out in 0.2 M $HClO_4$ at 20 °C. [d] Autocatalytic reactions; autocatalysis suppressed by addition of Eu(III) or V(III) (see ref 16). [e] $[H^+] = 0.20$ M, $\mu = 1.0$. [f] $[H^+] = 0.10$ M, $\mu = 1.0$. [g] See ref 14. [h] Reactions at 20 °C. [i] $[H^+] = 1.0$ M, $\mu = 2.5$. [j] $[H^+] = 0.20$ M, $\mu = 2.0$.

reductions of the basic form of this complex.[26] Analogous paths could conceivably contribute to reductions of the 2,4- and 2,5-isomers, but these would be overshadowed by the heavily predominant acid-independent components.

The Eu^{2+} reduction of the 2,3-isomer, which is complicated by very pronounced autocatalysis, exhibits the opposite acidity pattern; i.e., reduction is seen to be more rapid at higher acidities. Here, it appears that the "hard" Eu(II) center has once again spurned interaction with the ring nitrogen in favor of attack at the amide oxygen.[27,28] This is one of the very rare instances in which the acidity pattern for electron transfer can be reversed by alteration of the reductant;[29] a more extended examination of this system is being carried out.

The ligands from which complexes II–IV are derived readily undergo one-electron reduction when free.[24,30] When bound to Co(III), they would therefore be expected to favor an electron-transfer mechanism in which reduction of the bound ligand precedes reduction of the metal center (the so-called "chemical" or "radical-cation" mechanism).[3a,4,31] In such cases it may be asked whether the presumed radical-cation intermediate can be, in part, diverted. There is indeed evidence for such diversion[14] in the V^{2+} and Eu^{2+} reductions of analogues of dimer I in which the bridging group is an α-keto acid (e.g., pyruvato), rather than a pyridinecarboxylic acid. In the keto systems, dimerization of the intervening C–O type radical cation appears to compete with internal electron transfer to Co(III).[32] Reductions of dimers III and IV, however, are seen to yield Co(II) very nearly quantitatively (Table II), even with

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(26) Note that the Cr(II) value falls well below the corresponding bimolecular specific rates reported[6a] for the mono(carboxylato)-bridged dimers (15 M^{-1} s^{-1} for the 2-pyCOO derivative; 110 M^{-1} s^{-1} for the 4-pyCOO complex) neither of which suffers steric inhibition of conjugative interaction. Moreover, the V(II) value is less than the substitution-controlled upper limit[22,23] for inner-sphere reductions by this center.

(27) The increase in rate with acidity in this case may be attributed to the greater ease with which the protonated forms of pyridinecarboxamides undergo one-electron reduction.[28]

(28) See, for example: (a) Bruhlmann, U.; Hayon, E. *J. Am. Chem. Soc.* **1974**, *96*, 6169 (b) Fanchiang, Y.-T.; Gould, E. S. *Inorg. Chem.* **1978**, *17*, 1827.

(29) See, however: Loar, M. K.; Thomas, J. C.; Reed, J. W.; Gould, E. S. *Inorg. Chem.* **1977**, *16*, 2877.

(30) Fanchiang, Y.-T.; Thomas, J. C.; Neff, V. D.; Heh, J. C.-K.; Gould, E. S. *Inorg. Chem.* **1977**, *16*, 1942.

(31) (a) Diaz, H.; Taube, H. *Inorg. Chem.* **1970**, *9*, 1304. (b) Itzkowitz, M. M.; Nordmeyer, F. *Ibid.* **1975**, *14*, 2124.

(32) When the same keto-substituted dicobalt(III) dimers are reduced by Cr(II) or U(III), quantitative yields of Co^{2+} are obtained,[14] i.e., diversion of the radical intermediate no longer occurs, thus indicating that the intermediate is not the same as that intervening in reductions by Eu(II). It has been suggested that the Cr(III) or U(IV) center resulting from the initial act of electron transfer remains bound to the radical center whereas the very substitution-labile Eu(III) center escapes.

the reductant in deficiency, indicating that neither dimerization of the intermediate pyridyl-centered radical nor its disproportionation competes effectively with internal electron transfer. Since it is unlikely that pyridyl radical cations of the type under consideration undergo disproportionation at much lower specific rates than those for dimerization of $\dot{C}$–O radical cations,[33,34] we may infer that internal transfer to Co(III) in the pyridiyl radicals is significantly faster than that in the carbonyl radicals. What may be taken to be an analogous reactivity difference has been noted at the intermolecular level, for it has been shown[30] that $\dot{C}$–O radicals generated externally in aqueous solution reduce cobalt(III) complexes much less readily than externally generated pyridyl radicals having comparable formal potentials. A satisfactory explanation for this difference, either in the intra- or intermolecular mode, has not yet appeared.[35]

Of the oxidants featuring interrupted conjugation (V–VIII), that derived from $\text{Inic}^+\text{CH}_2\text{COOH}$ (V) deserves notice, for here values of k_{Cr}, k_{Eu}, and k_{U} are 10^2–10^4 times as great as those characteristic of outer-sphere reductions by these metal centers. It is difficult to conceive of any alternative to the radical-ion mechanism as the predominant path in these reductions, a conclusion in accord with our observation that the 3-CONH_2 isomer (VI), the ring system of which is reduced with much greater difficulty,[36,37] exhibits only marginal acceleration. Note also that internal electron transfer to Co(III) in the intermediate from oxidant V is very nearly quantitative (Table II), despite the break in conjugation.

Although the reducing cations may be assumed to attack the 4-CONH_2-substituted dimer, V, at its carbonyl group, we cannot say with confidence how the migrating electron makes its way to one of the Co(III) centers. We may inquire, as in earlier studies of monomeric $(\text{NH}_3)_5\text{Co}^{\text{III}}$ derivatives of this and related ligands,[8a] whether the electron is transmitted through space or through the series of bonds linking Co^{III} to the pyridine ring. Since rate enhancement for Cr^{2+} does not persist when the chain between the pyridine ring and the ligated carboxyl is lengthened from one to three atoms (oxidants VII and VIII), we suggest that through-bond transmission is predominant with this reductant. In contrast, we find substantial acceleration in the Eu^{2+} reduction of dimer VIII, in which the site of initial attack lies quite remote from the cobalt(III) centers, suggesting an important through-space contribution in this instance.[38–40]

Acknowledgment. The authors are grateful to Professor Karl Wieghardt, who stimulated initial interest in electron-transfer reactions of dimeric cobalt(III) complexes.

Registry No. II, 81704-85-0; III, 81704-88-3; IV, 81704-91-8; V, 81704-93-0; VI, 81704-95-2; VII, 81704-98-5; VIII, 81705-00-2; V, 7440-62-2; Cr, 7440-47-3; Eu, 7440-53-1; $\text{Ru(NH}_3)_6^{2+}$, 19052-44-9; U, 7440-61-1.

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(33) Disproportionations of nonligated pyridyl radicals in water have been shown to proceed at specific rates near the diffusion-controlled limit,[34] i.e., not appreciably more slowly than bimolecular reactions of carbonyl-derived radicals. Although such radical–radical reactions are doubtless retarded by ligation to the positive $\text{Co(OH)}_2\text{Co}$ unit, it is likely that such electrostatic effects are very nearly the same for both types of radicals.

(34) (a) Kosower, E. M.; Teuerstein, A.; Burrows, H. D.; Swallow, A. J. *J. Am. Chem. Soc.* **1978**, *100*, 5185. (b) Hayon, E.; Simic, M. *Ibid.* **1973**, *95*, 1029. (c) Singh, A. N.; Radlowski, C. A.; Reed, J. W.; Krishnamurthy, V. V.; Gould, E. S. *Inorg. Chem.* **1981**, *20*, 212.

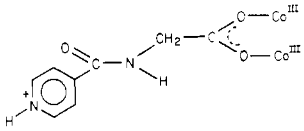
(35) It may perhaps be argued that deelectronation of a pyridyl radical entails less reorganization of molecular geometry and solvation shell than is the case for a carbonyl-derived radical, on which the "extra" electron is presumably more tightly localized.

(36) It is widely recognized[25,28a,37] that γ-CONH_2-substituted pyridyl radicals are considerably more stable than their β-substituted counterparts. This is presumed to be a conjugative effect—delocalization of the unpaired electron over both the carbamido carbon and the pyridine nitrogen is possible in the γ radical but not in the β.

(37) Cohen, H.; Meyerstein, D. *Isr. J. Chem.* **1974**, *12*, 1049.

(38) "Homoallylic" species, in which the reducing center is bound simultaneously to the carboxyl group and, through π-type interaction, to the pyridine ring, were proposed as intermediates in the reductions of (monomeric) $(\text{NH}_3)_5\text{Co}^{\text{III}}$ analogues of V, VIII, and related complexes.[8] Since the carboxyl function in the dimeric oxidants has been tied off by coordination to two Co(III) centers, such intermediates cannot be considered for the series at hand.

(39) Through-space interaction appears to be minimized in the case of the isonicotinylglycine oxidant, VII, probably because this amide derivative, like many known N-alkylated amides,[40] exists mainly in the trans conformer, IX.



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(40) See, for example: Robin, M. B.; Bovey, F. A.; Basch, B. In "The Chemistry of Amides"; Zabicky, J., Ed.; Wiley-Interscience: New York, 1970; pp 19–34.