Cr^{3+}–Cr^{2+} and Pz–Pz· potentials in the medium taken. Measurements by Fanchiang and co-workers[20] point to an apparent reduction potential for pyrazinecarboxamide (in 1.0 M $HClO_4$) very nearly the same as that for pyrazine itself which, from the data of Klatt and Rouseff,[21] may be assigned a value –0.020 V (vs. NHE). This, in combination with a Cr^{3+} potential of –0.41 V,[22] leads to an equilibrium constant of 3 × 10^{-7} for a redox reaction uncomplicated by chromium-pyrazine coordination. The discrepancy between this value and the observed constant, 3 × 10^{-8} M, indicates that the chromium(III)–radical complex is 10 times as stable toward heterolysis under our reaction conditions as is the (unobservable) chromium(II)–pyrazine complex, but in the absence of further information we cannot assign individual formation constants to these isomeric species.

Registry No. Cr, 7440-47-3; chloropyrazine, 14508-49-7; pyrazinetetracarboxylic acid, 43193-60-8; 2,3-pyrazinedicarboxylic acid, 89-01-0; methylpyrazine, 109-08-0; 2,6-dimethylpyrazine, 108-50-9; pyrazinecarboxylic acid, 98-97-5; pyrazine, 290-37-9; 2,5-dimethylpyrazine, 123-32-0; 2,6-dichloropyrazine, 4774-14-5; quinoxaline, 91-19-0; pyrazinecarboxamide, 98-96-4; (4-acetylpyridine)$(NH_3)_5Co^{3+}$, 59389-47-8; (4-benzoylpyridine)$(NH_3)_5Co^{3+}$, 42582-66-1; pyrazine$(NH_3)_5Co^{3+}$, 59389-55-8; fluoro$(NH_3)_5Co^{2+}$, 15392-06-0; chloro$(NH_3)_5Co^{2+}$, 14970-14-0; bromo$(NH_3)_5Co^{2+}$, 14970-15-1; iodo$(NH_3)_5Co^{2+}$, 15392-08-2.

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Electron Transfer. 31. Selectivity in Outer- and Inner-Sphere Reductions of Cobalt(III) by Uranium(III)[1]

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The specific rates of reduction, using U^{3+}, of a variety of organic derivatives of $(NH_3)_5Co^{III}$ are compared to those using other metal reducing centers. log k values for outer-sphere specific rates (25 °C, $\mu = 0.20$) are linearly related to the corresponding log k values for reductions with Cr^{2+}, V^{2+}, Eu^{2+}, and $Ru(NH_3)_6^{2+}$, each with near-unit slope, thus indicating that the Marcus model correlates the action of reductants having standard potentials differing by as much as 0.84 V. For such systems, kinetic selectivity is independent of both reactivity and thermodynamic driving force, in contrast to the situation prevailing for a wide variety of reaction series (featuring partial alteration of covalency in the activation process), for which the most reactive reagents are generally the least selective. Reductions of carboxylatocobalt(III) complexes are inner sphere. Here, again, log k_U values are linearly related to values of log k_{Cr}, log k_{Eu}, and log k_V, as well as to Taft's steric substituent parameters. However, selectivities of the various reducing centers differ, with U^{3+}, by far the *most* reactive, being somewhat more selective than Cr^{2+} and much more selective than Eu^{2+} and V^{2+}. It is suggested that the precursor complex for carboxylato-bridged U^{3+} reductions is analogous to that for Cr^{2+} reductions in that overlap is forbidden between the f_{xz^2} orbital, which holds the third 5f electron of U^{3+}, and the acceptor π orbital of the carboxylato group unless the ligand field of the metal center is unsymmetrically distorted by water molecules in the second coordination sphere, a process adversely affected by large lipophilic groups. For reductions with Eu^{2+}, however, overlap between the f_{z^3} orbital, which accommodates the seventh 4f electron, and the acceptor carboxyl orbital is symmetry permitted, and the susceptibility of reaction rate to the degree of chain branching drops sharply. Results of the present study indicate that, even in the absence of chelation or remote attack centers, selectivity patterns for inner-sphere reductions by f-electron centers are substantially different from those for d-electron centers, due primarily to the different symmetry character of the donor orbitals.

The report, in 1970, by Wang and Espenson[2a] that U^{3+} solutions in aqueous perchlorate media could be prepared and handled without unusual precautions added a powerful and versatile member to the array of reagents conveniently

Table I. Specific Rates for Uranium(III) Reductions of Cobalt(III) Complexes

Oxidant	$k_U{}^a$
Co(en)$_3{}^{3+}$	0.18
	0.22[b]
	0.133[c]
Co(NH$_3$)$_6{}^{3+}$	1.38
	1.32[c]
R(NH$_3$)$_5$Co^{III} [d] complexes	
R = imidazole	2.7
pyrazole	14
pyridine	26
dimethylformamide	33
N,*N*-dimethylnicotinamide	4.2×10^2
triethylacetato	6.3
trimethylacetato	42
cyclopentanecarboxylato	3.7×10^3
acetato	1.5×10^4 [c]
formato	8×10^4
lactato	7×10^4

[a] Specific rates for reductions by U^{3+} in M^{-1} s^{-1} at 25 °C; $\mu =$ 0.20 unless otherwise indicated. $[Co^{III}] = 3 \times 10^{-4}$–$6 \times 10^{-3}$ M. $[Co^{III}]/[U^{III}]_0 = 5$–20. Specific rates given are averages of four to eight replicate runs; agreement between runs was better than 8%. [b] $\mu = 0.35$. [c] See ref 3. [d] Structural formulas for heterocyclic ligands are given in Figure 1.

available for one-electron reductions. Shortly afterward, those workers presented evidence that oxidations of this tripositive actinide by Co(III) complexes could proceed by either an inner- or an outer-sphere path, depending upon the availability and nature of bridging ligands coordinated to the oxidizing center.[3] The present work, which deals principally with reductions of organic derivatives of (NH$_3$)$_5$Co^{III}, confirms and extends earlier conclusions and introduces additional information concerning the sensitivity of U(III) reductions to structural modification in the oxidant.

Experimental Section

Materials. Cobalt(III) complexes were available from previous studies[4] or were prepared as described;[4b,5] since traces of nitrate may lead to spurious results in kinetic studies involving U(III),[3] carbonatopentaamminecobalt(III) chloride,[4b] rather than the corresponding nitrate, was used as the starting material in these preparations. Uranium(III) solutions were made by dissolving dried U$_3$O$_8$ in warm perchloric acid and then reducing, under N$_2$, with zinc amalgam until the spectrum of the resulting olive green solution remained constant.[6] Agreement with spectral characteristics reported by Stewart[7] was excellent: λ_{max} 725 nm (ϵ 44), 667 (10), 635 (54), 614 (92), 522 (147), 506 (99), 450 (79), 350 (1560); lit. 725 (42.3), 668 (9), 635 (51), 615 (93), 522 (150), 507 (99), 451 (86), 349 (1590).[8]

Rate Measurements. Rates were estimated from absorbance decreases on a Cary 14 spectrophotometer[4,9] or a Durrum-Gibson stopped-flow spectrophotometer[10] as described. Measurements were made at 350 nm. Reactions were first order each in Co(III) and U(III), but rate measurements were carried out under pseudo-first-order conditions, most often with Co(III) in five- to twentyfold excess. Ionic strengths were adjusted to 0.2 M with HClO$_4$. Reactions were followed for at least 5 half-lives. Rate constants evaluated from successive half-life values within a single run generally agreed to within 5%. No trends indicative of systematic errors were observed, and average values did not differ significantly from those obtained from least-squares treatment of logarithmic plots of absorbance differences against reaction time. Specific rates obtained from replicate runs checked to within 8%. Temperatures were kept at 25.0 ± 0.2 °C during the entire series of experiments.

Results and Discussion

Kinetic data are summarized in Table I. Since none of the oxidants features a donor function which is appreciably protonated at [H$^+$] < 0.2 M,[11] acidity of the reaction medium was not varied in this study. If we include the reduction of (NH$_3$)$_5$CoN$_3{}^{2+}$ ($k = 1.1 \times 10^6$),[2a] specific rates for U^{3+}–
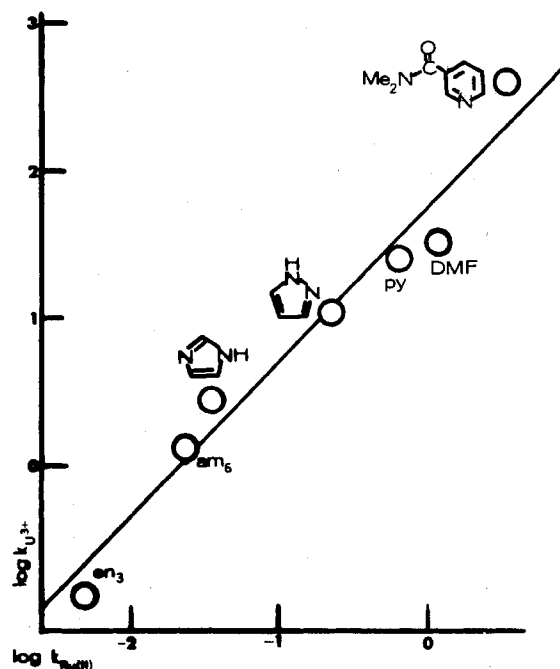

Figure 1. log–log plot comparing the specific rates of outer-sphere reductions of cobalt(III) complexes, listed in Table I, by U^{3+} ($\mu =$ 0.20; supporting electrolyte HClO$_4$) and Ru(NH$_3$)$_6{}^{2+}$ ($\mu = 0.50$; supporting electrolyte LiCl). The least-squares line shown corresponds to the equation log $k_U = 1.08$ log $k_{Ru} + 1.76$.

Co(III) reactions are seen to span a range of 10^7, about 3 decades narrower than the corresponding range for Cr^{2+} reductions and 2 decades less than that for Eu^{2+}. The lower end of the kinetic scale has been truncated for U^{3+} (i.e., there are no specific rates below 0.1 M^{-1} s^{-1}), doubtless reflecting the very high reducing potential ($E° = -0.63$ V) associated with this actinide center.

The first seven (noncarboxylato) oxidants in Table I, each of which lacks an effective[4a] "lead-in" group necessary for inner-sphere electron transfer, have been used to establish a pattern of relative outer-sphere rates which has been shown to apply to reductions by Cr^{2+},[9] Eu^{2+},[9] V^{2+},[4a] Ru(NH$_3$)$_6{}^{2+}$,[12] and a variety of organic radical centers not coordinated to metal ions.[13] Values of log k_U for these derivatives are plotted against the corresponding values of log k_{Ru} (referring to reductions by Ru(NH$_3$)$_6{}^{2+}$ in 0.50 M LiCl)[12,14] in Figure 1, a comparison which is of particular interest in view of the large difference between the potentials of the two reductants (0.84 V[15]). The resulting close approach to linearity and the near-unit slope of the regression line indicate that reductions by U^{3+}, like those by the dipositive metal centers, conform closely to the Marcus model;[16] i.e., differences in $\Delta G^{\ddagger}$ resulting from alteration of the ligand environment about Co(III) are independent of the reductant taken. Put another way, selectivity in outer-sphere reductions of cobalt(III) appears to be independent of both reactivity and thermodynamic driving force, in contrast to the situation prevailing for a wide variety of reaction series[17] which feature the partial making and/or partial breaking of bonds during the activation process. For series of the latter type, the most reactive reagents are generally the least selective.[18]

Wang and Espenson[3] reported that Co(NH$_3$)$_5$OAc^{2+} is reduced by U^{3+} over 10^4 times as rapidly as Co(NH$_3$)$_6{}^{3+}$. Since Fan[12] has shown that these two oxidants are reduced at very nearly the same rate in the absence of bridging, we may, with confidence, assign an inner-sphere mechanism to the U^{3+}–acetato reaction and, by implication, to the other carboxylato reactions in the present series as well.
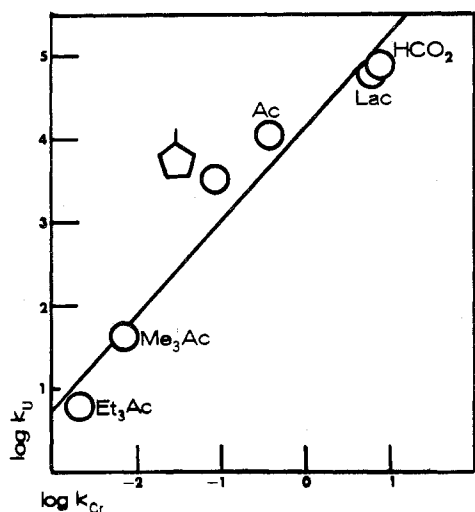
Figure 2. log–log plot comparing the specific rates of reduction of carboxylatopentaamminecobalt(III) complexes $R(NH_3)_5Co^{III}$, by U^{3+} ($\mu = 0.20$; supporting electrolyte $HClO_4$) and Cr^{2+} ($\mu = 1.0$; supporting electrolyte $LiClO_4$). Rate constants are at 25 °C; lac = lactato. The least-squares line shown corresponds to the equation $\log k_U = 1.14 \log k_{Cr} + 4.15$ with a correlation coefficient of 0.983.

Table II. Steric Susceptibilities for Carboxylato-Bridged Reductions of Cobalt(III) Complexes

Reductant	δ^a	Ref	Reductant	δ^a	Ref
V^{2+} (d^3)	0.31	4a	Eu^{2+} (f^7)	0.35	4b
Cr^{2+} (d^4)	0.69^b	4b, 21	U^{3+} (f^3)	0.89	This work

^{a} Steric susceptibility parameter, defined by Taft,[22] indicating the relative sensitivity of a given aliphatic reaction series to changes in the steric substituent parameters (E_s values) associated with groups attached to a reactant. ^{b} This value differs slightly from the earlier δ value,[21] based on more limited data available prior to 1966.

It has been emphasized[4b] that relative reactivities in inner-sphere series featuring organic ligands often depend markedly on the reductant taken, for inner-sphere rates are enhanced by additional conjugated lead-in sites and by chelating groups[19] which may coordinate selectively with the various reducing centers.[5,9,20] In the absence of such complicating substituents, log k values for one inner-sphere reductant may be linearly related to those for another,[4,5] but with nonunit slope. As seen in Figure 2, reductions of carboxylato derivatives of $(NH_3)_5Co^{III}$ with Cr^{2+} and U^{3+} conform to such a relationship (log k_U = 1.14 log k_{Cr} + 4.15), with the uranium reductions being somewhat more sensitive to structural alteration than the Cr^{2+} reductions.

Rates for oxidants of this type appear to be governed, in large part, by the severity of nonbonded interactions in the precursor, for values of log k associated with reductions by Cr(III),[21] V(II),[4a] and Eu(II)[4b] have been shown to be linear functions of Taft's steric substituent constants,[22] as in the case for the U^{3+}–carboxylato reactions in the present work.[23] Selectivities within these series may be compared using Taft's steric susceptibility parameters (δ values),[22] which indicate the sensitivity of specific rates within a series to the degree of ligand branching (Table II). Note that in this instance, *the most reactive reductant, U^{3+}, is the most selective.*

The observation that Cr^{2+} reductions are much more markedly affected by branching than are reductions by Eu^{2+} or V^{2+} has led to the suggestion[12] that because of the mismatch of orbital symmetry between the e_g orbitals of Cr^{2+} and the π orbitals of the carboxyl bridge, there will be minimal redox bridging unless there is unsymmetric distortion of the ligand environment about Cr(II) by interaction with water molecules
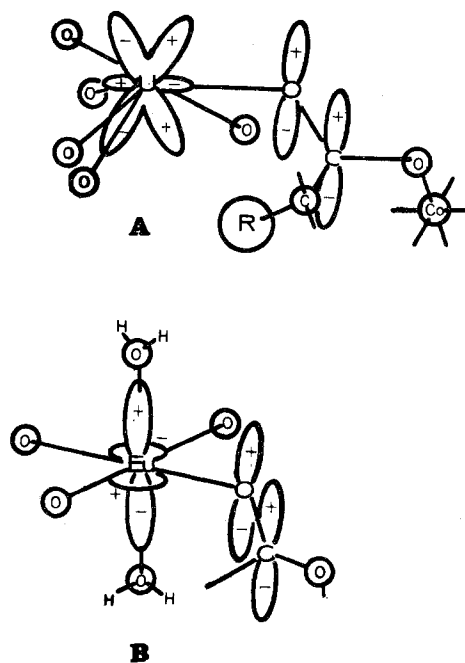

Figure 3. Precursor complexes for the inner-sphere reductions of a carboxylatocobalt(III) complex by (A) U^{3+} and (B) Eu^{2+}. Only six of nine ligands bound to U^{3+} are pictured. The reducing electron from U^{3+} is taken as arising from the f_{xz^2} orbital shown, whereas that from Eu^{2+} is represented as arising from f_{z^3}. Note the zero overlap between the donor orbital of U^{3+} and the acceptor π carboxyl orbital unless the coordination sphere of U(III) is subjected to distortion which is unsymmetric with respect to the carboxyl plane. In contrast, the f_{z^3}–π overlap in the Eu(II)–Co(III) precursor is favorable.

in the second coordination sphere, a process adversely affected by nearby lipophilic groups. Because the coordination geometries of Eu(II) and U(III) in solution are uncertain, extension of such reasoning to these reducing centers must be tentative, but a model in which U^{3+} assumes the nine-coordinated capped-prismatic configuration present in crystalline UCl_3 and UBr_3[24] may be considered reasonable. Splitting of the f orbitals in the appropriate D_{3h} field leads to five levels,[25] two of which are doubly degenerate. Comparison of orbital models with that of the prismatic coordination polyhedron indicates that the third 5f electron of U^{3+} will occupy the f_{xz^2} orbital indicated in Figure 3A. As shown, there will be zero overlap between this orbital and the acceptor orbital of the carboxylate group in the precursor complex unless the ligand field is unsymmetrically distorted.[9] In this sense, then, carboxylato-bridged reductions by U^{3+} may be considered analogous to those by Cr^{2+}, in accord with the similar susceptibilities which the two reducing centers exhibit to steric effects.

The octahedral configuration about Eu^{2+} in crystalline europium(II) oxide[26] suggests the occurrence of a coordination octahedron of water molecules (which present an "oxide-like" exterior to electropositive centers) about Eu^{2+} in aqueous solution. Octahedral splitting of the 4f orbitals[27] yields three levels, the two highest of which are triply degenerate. In Figure 3B, the reducing electron from Eu^{2+}, an f^7 center in the bridged precursor, is represented as arising from the f_{z^3} orbital shown (for which overlap between ligands and f-orbital lobe is maximal). The wave function for this orbital changes sign on passing through the carboxyl plane, as does that for the π orbital of the carboxyl group, and overlap in this case is symmetry permitted without distortion of the field. Thus, although rates in Eu^{2+}–Co(III) systems also are found to decrease with chain branching, the effect is a much more modest one and may merely reflect lower values for the

formation constant of the precursor.

In sum, symmetry barriers to electron transfer from octahedral d systems become operative when the electron arises from a high-energy (e_g) rather than a low-energy (t_{2g}) orbital, whereas, as a result of changes in coordination geometry and in the symmetry character of the donor orbitals, the reverse appears to be the case for f systems.

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Registry No. U(III), 22578-81-0; Co(en)$_3^{3+}$, 14878-41-2; Co-(NH$_3$)$_6^{3+}$, 14695-95-5; imidazole(NH$_3$)$_5$Co^{3+}, 38716-02-8; pyrazole(NH$_3$)$_5$Co^{3+}, 59389-55-8; pyridine(NH$_3$)$_5$Co^{3+}, 31011-67-3; dimethylformamide(NH$_3$)$_5$Co^{3+}, 31125-61-8; *N,N*-dimethylnicotinamide(NH$_3$)$_5$Co^{3+}, 31011-70-8; triethylacetato(NH$_3$)$_5$Co^{2+}, 51965-36-7; trimethylacetato(NH$_3$)$_5$Co^{2+}, 33887-25-1; cyclopentanecarboxylato(NH$_3$)$_5$Co^{2+}, 51965-54-9; acetato(NH$_3$)$_5$Co^{2+}, 16632-78-3; formato(NH$_3$)$_5$Co^{2+}, 19173-64-9; lactato(NH$_3$)$_5$Co^{2+}, 34464-03-4.

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Redox Chemistry of the Polyimine Complexes of Manganese(II), -(III), and -(IV) in Acetonitrile

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Electrochemical and spectroscopic studies have been made of the manganese(II), -(III), and -(IV) complexes formed by 2,2'-bipyridine, 1,10-phenanthroline, 2,2',2''-terpyridine, 4,4'-dimethyl-2,2'-bipyridine, 4,4'-diphenyl-2,2'-bipyridine, and 4,7-diphenyl-1,10-phenanthroline in acetonitrile solution. For both classes of complexes (bipyridine and phenanthroline) an irreversible oxidation of Mn(II) to Mn(III) occurs. The product species rapidly decomposes to form a dimeric manganese(III,IV) complex. Ultraviolet, visible, near-infrared, and electron paramagnetic resonance spectroscopies have been used to monitor species that are produced during electrolysis. The tridentate 2,2',2''-terpyridine ligand appears to prevent quantitative conversion of bis(2,2',2''-terpyridine)manganese(II) to a binuclear manganese(III,IV) complex. The tetrakis(1,10-phenanthroline)-di-μ-oxo-dimanganese(IV,IV) perchlorate complex has been prepared, and its reactivity with OH$^-$, Cl$^-$, and catechol has been studied.

Although manganese is an essential cofactor for photosynthetic oxygen evolution (photosystem II), its exact role and environment in the thylakoid membrane is unknown.[1,2] Several groups believe that the manganese system serves as a "charge collector" in photosystem II. After the accumulation of four equivalents of oxidizing power (via a four-photon sequential process), it rapidly oxidizes two water molecules[3-6]

$$2H_2O \xrightarrow{\text{[Mn]}} O_2 + 4H^+ + 4e^- \qquad (1)$$

Joliet and co-workers[7-10] have observed cooperation of photochemically produced intermediates of limited stability.

The proposed role of manganese in the buildup of oxidizing power has been based on the availability of higher oxidation states and variable coordination numbers.[11-13] Recent NMR relaxation experiments indicate that during the cyclic process photooxidation of Mn(II) to Mn(III) occurs, that the resting, dark-adapted system involves a mixed-oxidation-state manganese complex, and that the four-photon photoevent appears to involve four manganese ions.[14,15]

Other studies indicate that there are two types of manganese binding sites.[16-19] One form is bound to the interior of the