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Electron Transfer through Organic Structural Units. XIX. Rate Enhancement by Neighboring Groups in Reductions with Europium(II)[1]

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Specific rates of reduction, with Eu^{2+}, of 23 pentaamminecobalt(III) complexes (containing a variety of carboxylato groups) are compared to rates with Cr^{2+} and V^{2+}. Most values of k_{Eu} (25°, $\mu = 1.0$) lie near 1 M^{-1} sec^{-1}. Rates are remarkably insensitive to electronic effects, are enhanced slightly by neighboring –OR and –F groups, and are increased strongly by neighboring $-SO_3^-$. The V^{2+} and Eu^{2+} reductions of α,β-unsaturated complexes are slightly faster than those of aromatic complexes but, in contrast to reductions by Cr^{2+}, are generally acid independent, indicating that the variations in the Cr^{2+} series reflect medium effects rather than partial protonation of the carboxylato ligand. The present results add to growing evidence that Eu^{2+} reductions of carboxylatocobalt(III) complexes are, in large part, inner sphere.

Although the rapidity of substitution about europium(III) centers has to date prevented a direct demonstration of the inner-sphere mechanism for reductions by Eu(II), indirect evidence pointing to ligand bridging in the reduction of carboxylatocobalt(III) complexes is accumulating. Specific rates for a substantial series of such reductions have been found[2] to parallel the corresponding reductions with Cr(II), which have long been recognized to proceed with ligand transfer.[3] Moreover such reactions with Eu^{2+} proceed 10^1–10^5 times as rapidly as with $Ru(NH_3)_6^{2+}$, in contrast to the k_{Eu}/k_{Ru} ratio near 0.1 in instances where the structure of the oxidant rules out the inner-sphere path.[2] It has been noted that the various inner-sphere reductants respond with some selectivity to incorporation of neighboring groups into the carboxyl ligand; those donor groups which are "soft" in the Pearson sense[4] favor Cr^{2+} and Cu^+ over Eu^{2+},[2,5] whereas those which are hard favor reduction by the lanthanide center.

In the present extension of rate measurements in the Eu(II) series, we have encountered marked rate enhancement by the neighboring $-SO_3^-$ group. We also present data on reduction of α,β-unsaturated carboxylato complexes which point toward reinterpretation of an earlier study dealing with Cr(II) reductions.[6]

Experimental Section

Materials. Solutions of Eu(II),[2,7] Cr(II),[8] and V(II)[9] were prepared and analyzed as described. Carbonatopentaamminecobalt(III) chloride,[2] the corresponding nitrate,[8a] and lithium perchlorate[5] were prepared as described. Those cobalt(III) complexes not available from previous studies[2,5,6,8] were prepared from the aquopentaammine perchlorate in water[8a] or the carbonatopentaammine perchlorate in methanol[2] as described. Elemental analysis of complexes prepared here for the first time or those for which a check on purity was desired appear in Table I.

Rate Measurements. Rates were estimated from measurements of absorbance changes on the Cary 14 recording spectrophotometer as described.[2,7,8b] Measurements were made at 502 nm. Reactions were first order each in Co(III) and reductant, but rate measurements were generally carried out under pseudo-first-order conditions with at least a tenfold excess or reductant. For a number of complexes having uncoordinated donor sites or olefinic linkages, rates were followed at three or more acidities in the range 0.05–1.0 M H^+. Ionic strengths were adjusted to near unity by addition of twice-recrystallized $LiClO_4$. Reactions were followed for at least 5 half-lives. Rate constants evaluated from successive half-life values within a single run agreed to within 5%; no trends indicative of systematic errors were noted, 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%. No evidence for autocatalysis, as reported for related systems,[2,7,10] was obtained. Temperatures were kept at 25.0 ± 0.2° during the entire series of experiments.

Table I. Analyses of Pentaamminecobalt(III) Perchlorates, $RCo(NH_3)_5(ClO_4)_2$

	%, calcd			%, found		
R	C	H	Co	C	H	Co[a]
o-Hydroxycinnamato	21.34	4.30	11.5	21.18	4.19	11.4
p-Hydroxycinnamato	21.34	4.30	11.5	20.90	4.19	11.2
p-Fluorophenylacetato	19.30	4.23	11.8	19.25	4.23	11.8
β-Styrylacrylato	25.6	4.8	10.4	24.4	4.0	10.1

[a] See ref 8a.

Table II. Specific Rates for Europium(II), Chromium(II), and Vanadium(II) Reductions of Carboxylatopentaamminecobalt(III) Complexes, $R(NH_3)_5Co^{III}$ [a]

R	k_{Eu}	k_{Cr}[b]	k_V
Benzoato	0.83	0.15	0.59[g]
o-Iodobenzoato	0.78	0.095[e]	0.90[h]
o-Bromobenzoato	1.03	0.096[e]	
o-Chlorobenzoato	1.15	0.11[e]	0.57[h]
o-Fluorobenzoato	2.0	0.15[e]	0.72
p-Methoxybenzoato	0.78	0.19[e]	
o-Methylbenzoato	0.80	0.084	
5-Sulfosalicylato (I)	0.88		
Pentafluorobenzoato	1.10	0.08[f]	
p-Sulfobenzoato (II)	1.16	0.20	
o-Thiomethylbenzoato (III)	1.20	0.38[e]	0.75
m-Sulfobenzoato	1.43	0.22	
o-Fluorophenylacetato	1.67		
p-Fluorophenylacetato	1.10		
o-Methoxybenzoato	2.20	0.28[e]	0.60
o-Sulfobenzoato	7.40	0.50	2.5
Acetato[c]	1.97[d]	0.35	1.25[g]
Sulfoacetato (IV)	36	2.3	6.8
N,N-Dimethylnicotinamide (V)	0.45[i]	0.030	1.38[g]

[a] Specific rates in M^{-1} sec^{-1} at 25°. $\mu = 1.0$ unless otherwise indicated. Except for the acetato complex, reductions are with Eu(II) independent of (H^+) in the range 0.1–1.0 M. $(Co^{III})_0 = 7 \times 10^{-5}$–$1 \times 10^{-3}$ M. $(Eu^{II})/(Co^{III}) = 10$–$100$. Values for Eu(II) reductions are averages of three to five replicate runs; agreement between runs was better than 8%. [b] Specific rates for Cr^{2+} reductions taken from ref 3 and 8 unless otherwise indicated. [c] Limiting specific rate at low acidities. [d] $\mu = 4.0$. Experiments by Mrs. Jean Thomas. [e] $\mu = 3.0$. [f] A. Liang, Ph.D. Thesis, Kent State University, 1972. [g] See ref 10c. [h] R. T. M. Fraser, *J. Amer. Chem. Soc.*, **84**, 3436 (1962). [i] See ref 7.

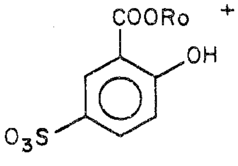
Results and Discussion

Rate constants for reduction by Eu^{2+} are assembled and compared to those by Cr^{2+} and V^{2+} in Tables II and III. The reduction of the acetato complex by each of the three metal centers is retarded at high acidities[2,10c,11] reflecting partial

Table III. Reductions of Alkenecarboxylatopentaamminecobalt(III) Complexes, $R(NH_3)_5Co^{III}$ [a]

R	$(H^+), M$	k_{Cr}	k_{Eu}	k_V
Acrylato	1.00	0.48	1.60	0.82
	0.10	0.52	1.70	0.87
m-Methoxycinnamato (VI)	1.00	0.75[b]	1.85	0.91
	0.10	1.09[b]	1.90	0.93
o-Hydroxycinnamato	1.00	0.77	1.92	0.85
	0.10	0.93	2.01	0.91
p-Hydroxycinnamato	1.00	0.60	2.24	0.78
	0.10	0.92	2.47	0.79
β-Styrylacrylato (VII)	1.00	0.96	2.00	0.89
	0.10	1.37	2.12	1.05

[a] Specific rates in M^{-1} sec^{-1} at 25°; $\mu = 1.0$. $(Co^{III})_0 = (2.4\text{–}3.0) \times 10^{-4}$ *M*. $(Eu^{II})/(Co^{III}) = 20\text{–}40$. Eu^{II} added to Co^{III}. Values for these reductions are averages of two to four replicate runs; agreement between runs was better than 6%. [b] $\mu = 1.20$ (see ref 6).



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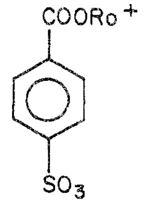

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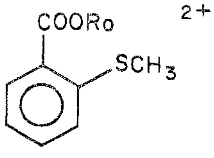
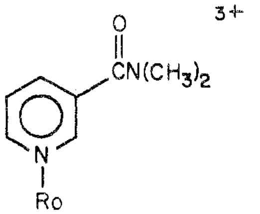


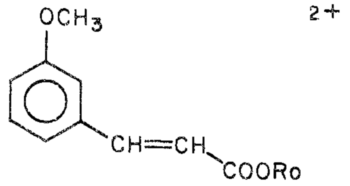
III

$O_3SCH_2COORo^+$

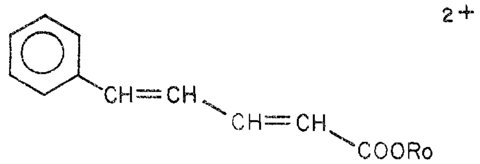
IV



V



VI



VII

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

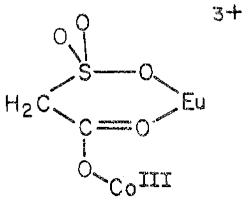
protonation of the carboxyl group, but the reductions of all other derivatives in Table II appear to be acid independent. Acid dependencies have been reported for reductions, by Cr^{2+}, of the unsaturated complexes in Table III.[6]

In the absence of chelating centers and a second conjugated function[3] values of k_{Eu} and k_{Cr} in the carboxylato series are linearly related[2]

$$\log k_{Eu} = 0.67 \log k_{Cr} + 0.54 \qquad (1)$$

The benzoato complex closely fits this relationship, and reasonable agreement is found also for many of the substituted benzoato derivatives having specific rates close to 1 M^{-1} sec^{-1} at 25° and $\mu = 1.0$. Indeed, as with reductions by Cr^{2+}, one is impressed with the insensitivity of the Eu^{2+} series to ring substitution. Even the attachment of five electron-withdrawing fluoro groups is nearly without effect, in contrast to the pronounced accelerations observed for outer-sphere reductions[2,12] when acid-strengthening substituents are incorporated into the oxidant.[13,14] Note further that the k_{Eu} carboxylato values are over twice that for the ring-bound *N,N*-dimethylnicotinamide complex (V), whereas with $Ru(NH_3)_6^{2+}$, for which reduction by the outer-sphere path is mandatory, members of the carboxylato series are reduced two orders of magnitude more slowly than oxidant V. Since other rate comparisons[2] rule out special accelerative effects in the reaction of complex V with $Ru(NH_3)_6^{2+}$, the nicotinamide–carboxyl rate reversal constitutes an additional point of evidence that a second and more facile path has become available for carboxylato reductions by Eu^{2+}, as well as by Cr^{2+}.

Values of k_{Eu} substantially greater than unity in Table II are associated only with those oxidants having a second donor group in a position favoring chelation. The effect is marginal for $-SCH_3$, small for both $-OCH_3$ and $-F$ (note the contrast with the k_{Cr} trends), but large with $-SO_3^-$.[15] Moreover, acceleration by sulfonate is seen to be much more marked for Eu^{2+} than for the other metal centers. Since it is unlikely indeed that the sulfonate function can facilitate internal electron transfer, rate enhancement almost certainly arises from an increase in the degree of formation of the precursor, which, for the sulfoacetato derivative may be represented as VIII.



VIII

Rate increases are less striking for the *o*-sulfobenzoato complex, which may form a chelated precursor featuring a seven-membered, but not a six-membered, ring.[16]

Values of k_{Cr} for the α,β-unsaturated complexes in Table III have been reported to decrease as (H^+) is increased from 0.01 to 1.2 *M* in perchlorate media (μ = 1.2),[6] and this variation has been taken as evidence for partition of each oxidant into a protonated (tripositive) and nonprotonated (dipositive) form, reduced at different specific rates. Since such a partition should be independent of the reductant, this interpretation predicts similar variations in rate for reductions by Eu^{2+} and V^{2+}. In the present work, values of k_{Cr} are again found to be acid dependent (although with a somewhat narrower range of variation than has been recorded for the higher ionicity), but, with the possible exception of complex VII, the corresponding trends are not observed for the other reductants. Since other protonation equilibria are not consistent with the reported kinetic picture,[17,18] it appears either that protonation of the oxidant does not change its rate of reaction with Eu^{2+} or V^{2+} or, alternatively, that the variations in the Cr(II) series reflect medium effects, similar to, but more intense than, those reported for the Cr^{2+} reduction of $(NH_3)_5H_2OCo^{3+}$.[19]

We lean strongly toward the latter view, which implies that inner-sphere reductions by Cr^{2+} should be significantly more sensitive than those by Eu^{2+} and V^{2+} to variations in the second coordination sphere of the reductant and beyond. This picture is in keeping with the suggestion[2] that because of this mismatch of orbital symmetry between the acceptor π orbitals of the carboxyl bridge and the reducing electron of Cr^{2+}, electron transfer requires an unsymmetric distortion of the ligand environment about Cr^{2+} in which water molecules in the second coordination sphere play a part. This mismatch extends neither to V^{2+} (which transfers a t_{2g} electron) nor to the 4f electron lost from Eu^{2+}. However, we cannot as yet say why such medium effects are more pronounced for the derivatives of α,β-unsaturated acids than for aliphatic or aromatic complexes.

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Registry No. (Benzoato)$(NH_3)_5Co^{III}$, 30931-77-2; (*o*-iodobenzoato)$(NH_3)_5Co^{III}$, 31060-39-6; (*o*-bromobenzoato)$(NH_3)_5Co^{III}$, 31060-38-5; (*o*-chlorobenzoato)$(NH_3)_5Co^{III}$, 52950-67-1; (*o*-fluorobenzoato)$(NH_3)_5Co^{III}$, 46503-45-1; (*p*-methoxybenzoato)$(NH_3)_5Co^{III}$, 52950-68-2; (*o*-methylbenzoato)$(NH_3)_5Co^{III}$, 30931-78-3; (5-sulfosalicylato)$(NH_3)_5Co^{III}$, 52950-70-6; (pentafluorobenzoato)$(NH_3)_5Co^{III}$, 52950-69-3; (*p*-sulfobenzoato)$(NH_3)_5Co^{III}$, 31060-43-2; (*o*-thiomethylbenzoato)$(NH_3)_5Co^{III}$, 51965-42-5; (*m*-sulfobenzoato)$(NH_3)_5Co^{III}$, 52950-71-7; (*o*-fluorophenylacetato)$(NH_3)_5Co^{III}$, 52950-72-8; (*o*-methoxybenzoato)$(NH_3)_5Co^{III}$, 31083-91-7; (*p*-fluorophenylacetato)$(NH_3)_5Co^{III}$, 52950-73-9; (*o*-sulfobenzoato)$(NH_3)_5Co^{III}$, 31060-45-4; (sulfoacetato)$(NH_3)_5Co^{III}$, 31083-92-8; (acrylato)$(NH_3)_5Co^{III}$, 44982-34-5; (*m*-methoxycinnamato)$(NH_3)_5Co^{III}$, 52993-09-6; (*o*-hydroxycinnamato)$(NH_3)_5Co^{III}$, 46913-88-6; (*p*-hydroxycinnamato)$(NH_3)_5Co^{III}$, 46922-32-1; (β-styrylacrylato)$(NH_3)_5Co^{III}$, 52950-74-0; europium(II), 16910-54-6; vanadium(II), 15121-26-3.

References and Notes

(1) Sponsorship of this work by the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

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(13) The rationale invoked by several workers[12,14] to account for the inverse relationship between basicity of oxidant-bound ligands and rate of outer-sphere electron transfer, to Co(III), which focuses on the energy of the d_{z^2} orbital on cobalt into which the electron moves, should, in principle, apply to inner-sphere reactions as well. The Co(III)–Cr(II) inner-sphere case, however, is complicated by bonding of the bridge to both metal centers in the precursor complex, and any structural modification of the bridge that will stabilize the d_{z^2} orbital on Co(III) should also stablize the d_{z^2} orbital on Cr(II), but to a lesser degree. Moreover, electron-withdrawing substituents on the bridging ligand would be expected to lower the formation constant of the precursor complex although increasing the specific rate of internal electron transfer.

(14) P. Benson and A. Haim, *J. Amer. Chem. Soc.*, **87**, 3826 (1965).

(15) Since specific rates for Cr^{2+} reductions of each of the sulfo complexes have been found to be independent of acidity,[8b] it is assumed that only the $-SO_3^-$ (unipositive) form of each of these derivatives is present in kinetically significant quantities.

(16) It is not unreasonable to relate the observed rate enhancement in Eu^{2+} reductions by the sulfonate group (which presents a "sulfate-like" exterior to outside species) to the relatively strong Eu(II)–sulfate interaction that is reflected in the large crystal energy (hence the limited solubility in water) of $EuSO_4$. Although such a relationship may be descriptively useful, it is obviously too rough to serve as a basis for a quantitative treatment.

(17) Values of k_{Cr} for the unsaturated complexes reach maximum limiting values at (H^+) near 0.02 M,[6] thus ruling out a kinetically significant contribution involving the conjugate acid of $Cr^{2+}(aq)$ ($pA_A > 9$).[18] The apparent kinetic saturation effect is likewise incompatible with the deprotonation of a Co(III)–Cr(II) binuclear precursor unless the formation constant for this precursor is large. In the latter event, however, the reduction would, contrary to experiment, no longer be first order in that reagent taken in excess.

(18) Although pK_A of $Cr(H_2O)_6^{2+}$ does not appear to have been recorded, we estimate a value near 11 from the known pK_A's of $Mg(H_2O)_6^{2+}$ (11.4) and $Mn(H_2O)_6^{2+}$ (10.6) [see, for example, F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967, p 32]. "Referee 2" suggests a value 1–2 units lower, reflecting the tetragonal distortion of Cr(II).

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Trans Effect in Octahedral Complexes. I. Rates of Ligation of *trans*-(Sulfinato-*S*)methanolbis(dimethylglyoximato)cobalt(III) Complexes in Methanol

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The rates of ligation of *trans*-(*p*-toluylsulfinato-*S*)methanolbis(dimethylglyoximato)cobalt(III) and *trans*-(methylsulfinato-*S*)methanolbis(dimethylglyoximato)cobalt(III) by thiourea, *p*-toluidine, pyridine, di(*n*-propyl) sulfide (*p*-toluyl complex only), triphenylphosphine, triphenylarsine, and triphenylstibine in methanol to produce the respective trans-ligated complexes have been investigated. Temperature dependencies for eight of these thirteen reactions are reported, as are solvent dependenices for selected systems. For all systems the reaction rate is first order in the cobalt complex, the net reaction proceeding to a measurable equilibrium state with entering ligands di(*n*-propyl) sulfide, triphenylarsine, and triphenylstibine. For ligand concentrations less than 0.06 F, the observed first-order rate parameter, k^{obsd}, depends upon [L] according to the relation $k^{obsd} = a + b[L]$. Nonzero values of a are only observed for systems which proceed to an equilibrium state, all values of b fall within the range $(3.7-18.2) \times 10^{-2}\ F^{-1}\ sec^{-1}$ at 25°, and all measured values of ΔH_b^* fall within the range 20.0–25.5 kcal/mol. At higher concentrations of L the rate law takes the form $k^{obsd} = (a + b[L])/(1 + c[L])$ where for the *p*-toluyl complex $c = 0.56 \pm 0.05$ and $0.40 \pm 0.05\ F^{-1}$ for thiourea and *p*-toluidine, respectively. This and other evidence are interpreted in favor of the ligation reactions proceeding *via* a limiting SN1 mechanism, although a prior association mechanism cannot be ruled out. Comparisons with previously studied systems show that in the title complexes S-bonded sulfinato ligands produce a moderate trans-labilizing effect; the relative ordering of trans-labilizing ability is $CH_3^- > SO_3^{2-} \gg RSO_2^- \gg I^- \simeq NO_2^-$. Evidence is presented which indicates that ligands which exert a kinetic trans effect in cobalt(III) complexes do so at least partially *via* a ground-state weakening of the trans bond.

Introduction

It is now well established that in cobalt(III) chemistry S-bonded sulfite produces a specific and dramatic labilization of the ligand situated trans to it.[2] Studies of several *S*-sulfitocobalt(III) systems have established that the mechanism involved in this process is probably SN1 in character, but no comprehensive theory is yet available to rationalize the phenomenon.[2] In an effort to provide such a rationalization, we set out to determine whether trans labilization occurs in cobalt(III) complexes for S-bonded ligands other than SO_3^{2-}.