ever, the reaction of dilute HNO_2 and *trans*-$[Co(OH_2)(NCO)(DH)_2]$ resulted in the formation of only *trans*-$[Co(NO_2)(NH_3)(DH)_2]$. Presumably the HNO_2 concentration was too low to compete effectively with the hydrolysis path.

In summary, this study provides evidence that the reactions of coordinated cyanate parallel the reactions of organic isocyanates, that carbamic acid can be stabilized relative to the free acid by coordination to a metal ion, that nitrosation of the coordinated cyanate proceeds *via* a carbamate intermediate, and that linkage isomerization occurs with coordinated carbamate. Also there is additional evidence for the $(NH_3)_5Co^{3+}$ intermediate.

Acknowledgment. A. M. S. expresses his gratitude to Professor Jannick Bjerrum, Claus Schaffer, and the University of Copenhagen for their hospitality in Chemistry Department I, during which some preliminary (nitrosation) experiments were conducted, and to Solveig Kallesoe for assistance at that time. We are also indebted to the Microanalytical Unit at the Australian National University and F. Bergerson and G. Turner, CSIRO, Canberra, for some ^{18}O analyses.

Appendix

The purpose of this Appendix is to show conditions under which systems of two consecutive reactions

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C \qquad \text{(A1)}$$

will give a linear plot of log $(A_t - A_\infty)$ *vs.* t, where A_t, A_∞, and t have been defined previously.

For eq A1 the concentrations of the species are given by

$$[A] = A_0 e^{k_1 t} \qquad \text{(A2)}$$

$$[B] = \frac{A_0 k_1}{k_2 - k_1}(e^{-k_1 t} - e^{k_2 t}) \qquad \text{(A3)}$$

$$[C] = A_0[1 + \frac{1}{k_1 - k_2}(k_2 e^{-k_1 t} - k_1 e^{-k_2 t})] \qquad \text{(A4)}$$

where A_0 is the initial concentration of A.

The absorbance of the reaction solution at time t is given by

$$A_t = \epsilon_a l[A] + \epsilon_b l[B] + \epsilon_c l[C] \qquad \text{(A5)}$$

where ϵ_a, ϵ_b, and ϵ_c are the molar extinction coefficients of species A, B, and C, respectively, and l is the spectrophotometer cell length in centimeters. Subsituting eq A2, A3, and A4 into eq A5 and collecting terms in $e^{-k_1 t}$ and $e^{-k_2 t}$ results in

$$A_t - A_\infty = lA_0[\frac{(k_2\epsilon_a - k_1\epsilon_a + k_1\epsilon_b - k_2\epsilon_c)}{k_2 - k_1}e^{-k_1 t} + \frac{k_1}{k_2 - k_1}(\epsilon_c - \epsilon_b)e^{-k_2 t}] \qquad \text{(A6)}$$

where

$$A_\infty = \epsilon_c l A_0 \qquad \text{(A7)}$$

Rearranging and factoring the first term gives

$$A_t - A_\infty = \frac{lA_0}{k_2 - k_1}[(k_2 - k_1)(\epsilon_a - \epsilon_c) - k_1(\epsilon_c - \epsilon_b)]e^{-k_1 t} + \frac{lA_0 k_1}{k_2 - k_1}(\epsilon_c - \epsilon_b)e^{-k_2 t} \qquad \text{(A.8)}$$

Inspection of eq A8 shows the following conditions allow a near-linear plot of log $(A_t - A_\infty)$ *vs.* t: (1) $k_1 >> k_2$ or $k_2 >> k_1$; (2) $\epsilon_b = \epsilon_c$; (3) $k_1/k_2 = (\epsilon_c - \epsilon_a)/(\epsilon_b - \epsilon_a)$.

Registry No. $(NH_3)_5CoNCO^{2+}$, 19998-52-8; $(NH_3)_5CoNH_2CO_2H^{3+}$, 52133-51-4; $(NH_3)_5CoO_2CNH_2^{2+}$, 19173-65-0; $(NH_3)_5CoNHCO_2H^{2+}$, 52133-52-5; $[(NH_3)_5CoNCO](ClO_4)_2$, 27427-52-7.

Contribution from the Department of Chemistry,
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Electron Transfer through Organic Structural Units. XVI. Reductions of Carboxylatopentaamminecobalt(III) Complexes with Europium(II)[1]

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The specific rates of reduction of 53 pentaamminecobalt(III) complexes (containing a variety of carboxylato groups) with Eu^{2+} and Cr^{2+} are compared. The Eu(II) rates span a range of almost 10^7, but over half fall in the interval 0.8-2.0 M^{-1} sec^{-1}. Specific rates much less than unity are encountered with complexes bearing bulky ligands. For oxidants in this category, rates with the two reducing centers fit the relationship $\log k_{Eu} = 0.67 \log k_{Cr} + 0.54$, the slope of the regression line being significantly less than unity, the value observed for outer-sphere reductions. Reductions with Eu^{2+} are disproportionately accelerated by neighboring hydroxy, alkoxy, fluoro, and sulfonate groups, in contrast to the reactions of Cr^{2+}, for which rate enhancements are more marked when neighboring substituents feature the softer sulfur and nitrogen donor centers. The acidity dependence by the acetato complex leads to a specific rate of 0.25 M^{-1} sec^{-1} for the reduction, probably by an outer-sphere path, of the protonated form of this derivative. A number of the inverse acid paths observed for Cr^{2+} reductions of complexes having a neighboring COOH group disappear with Eu^{2+}. For three of the complexes, each having a CHO group remote from, but conjugated with, $COOCo^{III}$, the rate law for reduction with Eu^{2+} includes a term first order in H^+. Experience with other reductants indicates that these reactions proceed, at least in part, by initial Eu^{2+} attack at CHO. This remote path is much less facile for Eu^{2+} than for Cr^{2+}. The observed patterns support the view that the several variants of the inner-sphere mechanism which have been defined for Cr^{2+} extend also to Eu^{2+} and that mediating paths or chelating functions featuring hard donor centers especially favor reductions by Eu^{2+}.

Aside from reductions by Cr^{2+}, which center may be considered the prototype inner-sphere reductant,[2] strong evidence

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[1] Sponsorship of this work by the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

[2] (a) H. Taube, H. Myers, and R. L. Rich, *J. Amer. Chem. Soc.*, 75, 4118 (1953); (b) H. Taube and H. Myers, *ibid.*, 76, 2103 (1954); (c) H. Taube and E. S. Gould, *Accounts Chem. Res.*, 2, 321 (1969).

for bridged paths has been obtained for certain reductions by V^{2+},[3] Cu^{+},[4] and Fe^{2+} [5] and rather less compelling indications of such mechanisms for reductions by U^{3+} and Yb^{2+}.[6] There is, however, considerable doubt as to the part the inner-sphere route plays in reductions of Eu^{2+}. The substitution-labile character of the Eu(III) products militates against direct proof, and indirect evidence is uncertain. The rates of reduction, by Eu^{2+}, of halogen-substituted oxidizing metal centers have been found[7] to be quite sensitive to the identity of the halo ligand, but Dockal,[8] in examining the reductions of $(NH_3)_5Co^{III}$ derivatives of heterocyclic bases, reported that those ligands which most markedly favor bridging in reductions by Cr^{2+} are without substantial effect with Eu^{2+}.

Kinetic patterns for reductions by Cu^{+} and V^{2+} suggest[3d,4b] that Pearson's description of donors and acceptors as hard and soft reagents[9] may have some applicability to electron-transfer reactions and that inner-sphere paths are most favored when the lead-in donor atom (or a nearby chelating center) and the reducing center are complementary donor-acceptor pairs. If so, inner-sphere reductions by the "hard" Eu^{2+} cation should be more likely to occur through a "hard" carboxyl lead-in group than through a "softer" group in which the donor atom is sulfur or nitrogen.

Although specific rates for Eu^{2+} reductions of several carboxylato derivatives of $(NH_3)_5Co^{III}$ have been reported,[10] the present study appears to be the first in which a sufficient number of oxidants are taken to allow reactivity patterns to emerge. Our impression is that these patterns are similar enough to those for the corresponding reductions with Cr^{2+} to indicate that reductions of Eu^{2+} in this series, like those by Cr^{2+},[2c] are, in large part, inner sphere.

Experimental Section

Materials. Chloropentaamminecobalt(III) perchlorate,[11a] chromium(II) solutions,[11] and lithium perchlorate[4b] were prepared as described. Europium(III) perchlorate was prepared in solution by dissolving 99.9% Eu_2O_3 (Alfa) in an equivalent quantity of $HClO_4$ and filtered to remove traces of residue. Reduction of $Eu(ClO_4)_3$ was carried out by reduction with zinc amalgam in 0.1 *M* $HClO_4$.[11b] The concentrations of Eu(II) and Cr(II) in the respective solutions were determined as described.[8,11a]

Carbonatopentaamminecobalt(III) chloride was prepared by dissolving 58 g of powdered ammonium carbonate in 60 ml of water and 100 ml of concentrated aqueous ammonia, adding a solution of 30 g of $CoCl_2 \cdot 6H_2O$ in 40 ml of water, and then bubbling air very slowly through the mixture (20 bubbles/min) for 2 days. The solution was cooled to 0°, and 600 ml of methanol was added slowly with stirring. The preparation was kept at 0° for 3 days, and the precipitated carbonato chloride was filtered off. This was purified by dissolving in twice its weight of water, adding LiCl (1 g of LiCl/2 g of complex), filtering, and then slowly adding an equal volume of methanol. The solution was kept at 0° for 10 hr, and the crystalline complex was filtered off and dried *in vacuo*. This procedure is more convenient than the method of Kranig,[12] of which it is an adaptation, and gives a purer product.

Anal. Calcd for $Co(NH_3)_5CO_3Cl$: C, 5.01; H, 6.27. Found: C, 4.82; H, 6.16.

The carbonato chloride was converted to the carbonato perchlorate by dissolving in a minimum volume of water, adding an equal volume of saturated $LiClO_4$, cooling to 0°, and filtering of the crystals formed. Either carbonato complex could be converted to aquopentaamminecobalt(III) perchlorate by treatment with aqueous $HClO_4$ as described.[11a]

Carboxylato Complexes. A number of the complexes were available from previous studies.[3d,4b,11b] When the complete absence of nitrate was desired (in order to rule out the consumption of Eu^{2+} by NO_3^- in subsequent kinetic experiments), complexes were prepared, as their perchlorates, from samples of the aquo perchlorate[11a] or the carbonato perchlorate[4b] which were, in turn, derived from the carbonato chloride, as described above, rather than from the carbonato nitrate.

In addition, a newer procedure was particularly useful for cases in which parent acid and its lithium (or sodium) salt are soluble in methanol. In this modification, 10 mmol of the acid and 5 mmol of LiOH (or NaOH) were added to 20 ml of absolute methanol, and to the mixture was added 400 mg of finely ground carbonatopentaamminecobalt(III) perchlorate. The mixture was refluxed for 2 hr with frequent shaking. The preparation was cooled to 0°, and 1.0 ml of concentrated $HClO_4$ was added, after which the preparation was kept at 0° for an additional 30 min. The precipitate, if any, was filtered off and washed with ether. The mother liquor was shaken with 150 ml of ether, generally precipitating an additional portion of the desired complex. The combined crude products were recrystallized from a minimum volume of hot water and then dried *in vacuo*. Yields ranged from 40 to 80%, and contamination with the parent carboxylic acid was often much less serious than for preparations in water[11a] or in diethylene glycol.[4b] This method was also applicable to the preparation of the complex of 2,4-dinitrophenol, which is, to our knowledge, the first phenol-coordinated $(NH_3)_5Co^{III}$ complex reported.[13-15] Carbon, hydrogen, and cobalt analyses of complex perchlorates prepared by this method were in agreement with calculated values.[16]

Rate Measurements. Rates were estimated from measurements of absorbance changes on the Cary 14 recording spectrophotometer[8,11b] or on the Durrum-Gibson stopped-flow spectrophotometer.[17] Measurements were made at 502 nm, the low-energy absorption maximum for the Co^{III} complexes. Except as noted below, reactions were first order each in Co(III) and in reductant, but rate

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(3) (a) H. J. Price and H. Taube, *Inorg. Chem.*, 7, 1 (1968); (b) K. W. Hicks, D. L. Toppen, and R. G. Linck, *ibid.*, 11, 310 (1972); (c) C. Norris and F. R. Nordmeyer, *ibid.*, 10, 1235 (1971); (d) J. C. Chen and E. S. Gould, *J. Amer. Chem. Soc.*, 95, 5539 (1973).

(4) (a) O. J. Parker and J. H. Espenson, *J. Amer. Chem. Soc.*, 91, 1968 (1969); (b) E. R. Dockal, E. T. Everhart, and E. S. Gould, *ibid.*, 93, 5661 (1971).

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(8) E. R. Dockal and E. S. Gould, *J. Amer. Chem. Soc.*, 94, 6673 (1972).

(9) See, for example, R. G. Pearson Ed., "Hard and Soft Acids and Bases," Dowden, Hutchison, and Ross, Stroudsburg, Pa., 1973.

(10) See, for example: (a) R. T. M. Fraser, *J. Amer. Chem. Soc.*, 84, 3436 (1962); (b) A. Zanella and H. Taube, *ibid.*, 94, 6403 (1972).

(11) (a) E. S. Gould and H. Taube, *J. Amer. Chem. Soc.*, 86, 1318 (1964); (b) E. S. Gould, *ibid.*, 87, 4370 (1965); 88, 2983 (1966).

(12) J. Kranig, *Bull. Soc. Chim. Fr.*, [4] 43, 992 (1928).

(13) Occasional variation of conditions for the reaction in methanol was necessary. For the malonato and mucochlorato preparations, no LiOH or NaOH was used; the reaction volume for the former was 80 ml. For the pyruvato and benzoylformato preparations, the reaction temperature was 55-60°, and for the mucochlorato, 50°. In evaluating the several methods for preparing $(NH_3)_5Co^{III}$ derivatives of carboxylic acids, we recommend the preparation from the aquo complex in water[11a] for complexes of such very polar ligands as pyridine- and pyrazinecarboxylic acids and SO_3H-substituted acids. When both the acid and its sodium (or lithium) salt are soluble in water and in methanol, either the aquo preparation or the methanol preparation may be used, with the latter generally giving higher yields. When the acid is soluble in methanol, but not in water, the preparation in methanol gives the more satisfactory product. For lipophilic acids which are sparingly soluble in both methanol and water, preparation from the carbonato complex in diethylene glycol[4b] is the method of choice; this method is also suited to aminobenzoic acids, amido-substituted acids, and oxidizable acids which do not survive treatment with Co(III) in hot aqueous solutions. In our hands, previously described preparations from the dimethylformamido complex in DMF,[11b] from the carbonato complex in DMF,[14] and from the aquo complex and the carboxylic anhydride[15] were less successful.

(14) M. Z. Hoffman and M. Simic, *J. Amer. Chem. Soc.*, 92, 5533 (1970).

(15) L. M. Jackman, R. M. Scott, and R. H. Portman, *Chem. Commun.*, 1338 (1968).

(16) F.-R. F. Fan, M.S. Thesis, Kent State University, 1974.

(17) (a) M. B. Barrett, J. H. Swinehart, and H. Taube, *Inorg. Chem.*, 10, 1983 (1971); (b) E. S. Gould, *J. Amer. Chem. Soc.*, 96, 2373 (1974).

Table I. Yields of Co(II) from Reduction, Using Eu^{2+}, of Carboxylatopentaamminecobalt(III) Complexes[a]

Ligand	Yield of Co(II), %
Oxalato	100
Pyruvato	100
Formato	100
Acetato	100
Glutarato	99
Malonato	100
p-Formylcinnamato	100
Oxydiacetato	100
Mucochlorato	99
Glycolato	100
Fluoroacetato	100
Benzoato	99
Salicylato	99
p-Formylbenzoato	100
o-Nitrobenzoato	42
p-Nitrobenzoato	27
m-Nitrobenzoato	10
2,6-Pyridinedicarboxylato	100

[a] $[H^+] = 1.0\ M$; $[Co(III)] = 0.02\ M$; $[Eu(II)] = 0.014\ M$; Eu(II) added to Co(III).

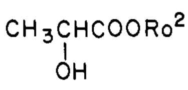
measurements were generally carried out under pseudo-first-order conditions with at least tenfold excess of reductant. For a number of complexes having uncoordinated donor sites, rates were followed at three or more acidities in the range 0.05–1.0 M H^+. Ionic strengths were adjusted to near unity by 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 4%; no trends indicative of systematic errors were noted, and average values did not differ significantly from least-squares treatment of logarithmic plots of absorbance differences against reaction time. Specific rates obtained from replicate runs on the Cary checked to better than 7%, whereas successive oxidations (with the same pair of master solutions) were repeated on the Durrum until decay curves for three consecutive runs were superimposable. Specific rates obtained by stopped flow from different master solutions agreed to better than 5%. A few of the faster reactions were examined also under second-order conditions using equivalent quantities of reactants; specific rates in these cases were in agreement with those derived from the pseudo-first-order runs, although reproducibility between runs was poorer. Temperatures were kept at 25.0 ± 0.2° during the entire series of experiments.

Departures from straightforward kinetics were observed in the reductions of certain pyridinecarboxylato derivatives which exhibited autocatalytic behavior of the type previously reported.[18] In addition, the treatment of nitrobenzoato complexes with Eu^{2+} brought about a very rapid rise of absorbance in the 480–520-nm region, followed by a much slower fading, which appeared to have more than one kinetic component. Finally, rapid reduction of Co^{III} in the 2,6-pyridinedicarboxylato complex was followed by a much slower secondary reaction, presumably reflecting reduction of the pyridine ring system. However, the rate constant for the latter was approximately 0.01 times that of the initial reduction; hence, in this case, the two kinetic components were easily separable.

Stoichiometry Studies. Stoichiometry experiments, in which a deficiency of Eu^{2+} was treated with a number of carboxylato complexes, were carried out in a manner analogous to that earlier described for Cr^{2+} reductions.[11a] Results are presented in Table I. As noted earlier with Cr^{2+} reductions,[19] stoichiometry was sometimes erratic for complexes prepared from the carbonatopentaammine nitrate *via* the aquopentaammine perchlorate, due almost certainly to contamination by traces of nitrate. Reproducible results were obtained for complexes prepared from the carbonato chloride *via* the carbonato perchlorate.

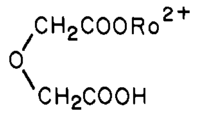
Results and Discussion

Range of Rate Constants. Rate constants for reduction by Eu^{2+} are assembled and compared to those for reduction by Cr^{2+} in Tables III and IV. Specific rates in Table II appear to be independent of (H^+) in the range 0.1–1.0 M, whereas those in Table III exhibit some variation with acidity. If we include such slowly reacting $(NH_3)_5Co^{III}$ complexes as the imidazole and pyrazole derivatives, for which $k_{Eu^{2+}}$ values at 25° lie near $10^{-2}\ M^{-1}\ sec^{-1}$,[8] the range of rate constants for Eu^{2+} is nearly 10^7, only a single decade narrower than that range for Cr(II).[2c] The tenfold advantage enjoyed by Eu^{2+} at the slow end of the scale is not potentiometric in origin[8] but stems, at least in part, from the proportionately less severe contraction of metal-water bonds at the larger reducing center preceding the act of electron

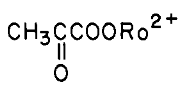


$CH_3CH(OH)COORo^{2+}$

I

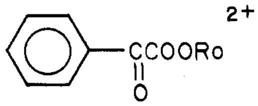


II



$CH_3C(=O)COORo^{2+}$

III



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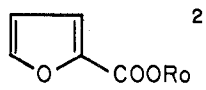

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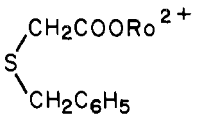

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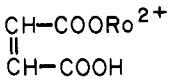
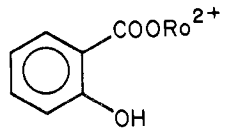
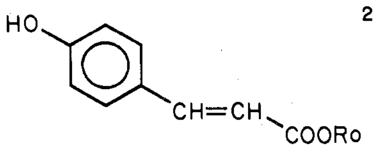


$CH(COORo)=CH(COOH)^{2+}$

VII



VIII



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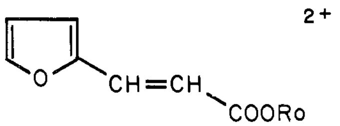
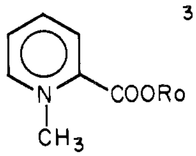


X



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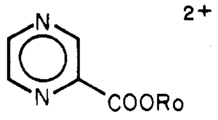
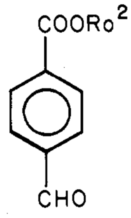
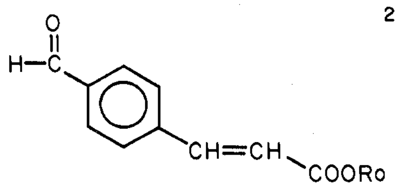


XII



XIII



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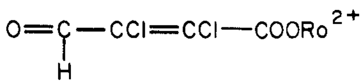
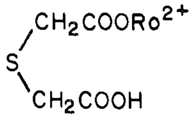


$O{=}CH{-}CCl{=}CCl{-}COORo^{2+}$

XV



XVI

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

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[18] (a) C. Norris and F. R. Nordmeyer, *J. Amer. Chem. Soc.*, 93, 4044 (1971); (b) J. R. Barber, Jr., and E. S. Gould, *ibid.*, 93, 4045 (1971).

[19] A. Liang and E. S. Gould, *Inorg. Chem.*, 12, 12 (1973).

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

R	$k_{Eu^{2+}}$	$k_{Cr^{2+}}$ [b]
Triethylacetato	0.068	0.0022
Trimethylacetato	0.163	0.0070
Di-*n*-propylacetato	0.29	0.036^c
Diethylacetato	0.34	0.047^c
Diphenylacetato	0.50	0.058^c
Phenylmethylacetato	0.53	0.057^c
Cyclopentanecarboxylato	0.74	0.093^c
Cyclohexylacetato	0.80	0.12^c
Cyclopropanecarboxylato	1.10	0.19^d
Propionato	1.19	0.173
Formato	15.4	7.2
Glycolato	88	3.1
Lactato (I)	91	6.7
o-Benzylglycolato	11	0.21^c
Oxydiacetato (II)	4.9×10^2	$0.22 + 0.0058/(H^+)^c$
Pyruvato (III)	1.15×10^3	10×10^3
Benzoylformato (IV)	3.7×10^4	
Furoato (V)	3.5	0.37
Acetoxyacetato	1.43	0.17
Fluoroacetato	3.8	0.118^c
Difluoroacetato	1.88	0.113^c
Trifluoroacetato	1.23	0.039^c
Trichloroacetato	0.82	
S-Benzylthioglycolato (VI)	1.84	5.3
Se-Benzylselenoglycolato	1.68	5.2
β-Benzylmercaptopropionato	1.05	
Malonato	17.0	*e*
1,1-Cyclobutanedicarboxylato	2.2	$0.20 + 0.093/(H^+)$
Succinato	2.18	0.17^f
Glutarato	1.29	
Maleato (VII)	4.5	200
Benzoato	0.84	0.15
p-Hydroxybenzoato	1.04	0.21
Salicylato (VIII)	0.84	$0.11 + 0.03/(H^+)$
o-Acetylbenzoato	0.99	0.72
o-Thiomethylbenzoato	1.10	0.35
o-Formylbenzoato	1.8	94
Biphthalato	1.60	$0.075 + 0.004/(H^+)$
Terephthalato	1.15	0.21
p-Hydroxycinnamato (IX)	1.97	1.12^g
o-Hydroxycinnamato	1.95	1.30^g
Furanacrylato (X)	0.84	1.36^g
3-Pyridinecarboxylato	1.34	0.13
N-Methyl-2-pyridinecarboxylato (XI)	1.06	0.087
2,6-Pyridinedicarboxylato	3.5×10^3	
Pyrazinecarboxylato (XII)	3.6×10^3	

[a] Specific rate in M^{-1} sec^{-1} at 25°; $\mu = 1.0$. Reductions with Eu^{2+} 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^{2+} reductions are averages of two to five replicate runs; agreement between runs was better than 7%. [b] Specific rates for Cr^{2+} reductions taken from ref 11 and 17 unless otherwise indicated. [c] This work. [d] $\mu = 3.0$. [e] $k_{Cr^{2+}}$ for this complex at $\mu = 4.0$ and $(H^+) > 1.0$ M reported as 4.2 M^{-1} sec^{-1}: C. Lavallee and E. Deutsch, *Inorg. Chem.*, 11, 3133 (1972). Specific rate reported as $0.34 + 1.08/(H^+)$ at $\mu = 1.0$ and lower acidities: G. Svatos and H. Taube, *J. Amer. Chem. Soc.*, 83, 4172 (1961). [f] At 14.1°: D. K. Sebera and H. Taube, *J. Amer. Chem. Soc.*, 83, 1785 (1961). [g] Limiting specific rates at low acidities (see ref 19).

transfer.[20] The upper kinetic limit is nearly the same for the two reductants and reflects the joint operation of a diffusion-controlled maximum of $10^{9.8}$ M^{-1} sec^{-1} for bimolecular reactions in water[21] at 25° and an activation entropy requirement more negative than −25 eu[22] (corresponding to a rate diminution of $10^{5.4}$) which appears to be associated with non-substitution-limited redox reactions of this charge type, irrespective, with but a few exceptions,[23] of structural details. Certain of the kinetic acidity patterns reported for Cr^{2+} persist also with Eu^{2+}, but they are generally subdued. For no oxidant is an acid dependency observed with Eu^{2+}, but not with Cr^{2+}. Just as a large number of Cr^{2+} reductions in the carboxylato series exhibit specific rates between 0.12 and 0.30 M^{-1} sec^{-1},[11a] so also do many of the Eu^{2+} values fall in the range 0.8–2.0 M^{-1} sec^{-1}. Rate constants for Eu^{2+} reductions much above this range point to the operation of rate-enhancing effects which appear to be similar to those observed with Cr^{2+}, whereas specific rates much less than unity are encountered when the carboxylato group presents severe steric demands.

Aliphatic Complexes. Eu^{2+}–Cr^{2+} Correlations and Steric Effects. Among redox series for which reactivity patterns

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[20] (a) See, for example, R. A. Marcus, *Annu. Rev. Phys. Chem.*, 15, 155 (1964). (b) An additional factor which should, in principle, favor Eu^{2+} is the similarity between the symmetry properties of the f orbital from which the reducing electron is lost and the π orbitals of the mediating unit, in contrast to the mismatch of symmetry when an e_g electron is lost from Cr^{2+}. [See, for example: J. C. Eisenstein, *J. Chem. Phys.*, 25, 142 (1956); H. G. Friedman, Jr., G. R. Choppin, and D. G. Feuerbacher, *J. Chem. Educ.*, 41, 354 (1964)]. Since, however, the kinetic advantage enjoyed by Eu^{2+} persists with outer-sphere oxidants,[8] this effect may be considered a minor one in the systems at hand.

[21] E. F. Caldin, "Fast Reactions in Solution," Wiley, New York, N. Y., 1964, p 12.

[22] R. G. Linck, *MTP (Med. Tech. Publ. Co.) Int. Rev. Sci.: Inorg. Chem., Ser. One*, 9, 303 (1972).

[23] (a) R. Farina and R. G. Wilkins, *Inorg. Chem.*, 7, 514 (1968); (b) N. Sutin, J. K. Rowley, and R. W. Dodson, *J. Phys. Chem.*, 65, 1248 (1961); (c) R. C. Patel and J. F. Endicott, *J. Amer. Chem. Soc.*, 90, 6364 (1968).

Table III. Kinetic Data for H^+-Dependent Europium(II) Reductions of Carboxylatopentaamminecobalt(III) Complexes

Organic ligand	$(H^+), M$	k^a
Acetato[b,c]	3.82	0.45
	3.00	0.54
	2.00	0.63
	1.00	0.94
	0.20	1.62
	0.096	1.97
p-Formylbenzoato (XIII)[b]	0.01	1.20
	0.10	1.20
	0.50	1.31
	2.0	1.58
	4.0	1.89
p-Formylcinnamato (XIV)	0.05	4.1
	0.10	4.5
	0.25	5.0
	0.50	5.5
	1.0	7.3
Mucochlorato (XV)	0.10	130
	0.20	186
	1.00	6.9×10^2
Oxalato	1.10	5.0×10^2
	0.05	1.9×10^3
Thiodiglycolato (XVI)	1.0	15.5
	0.20	17
	0.05	21
	0.01	47
2-Pyridinecarboxylato	1.0	2.2[d]
	0.10	2.9[d]
	0.050	3.3[d]

[a] Specific rates in M^{-1} sec^{-1} at 25°; $\mu = 1.0$ unless otherwise indicated. Reactions run under pseudo-first-order conditions with $(Eu^{II})/(Co^{III}) = 10$–$100$. $(Co^{III})_0 = 7 \times 10^{-5}$–$1 \times 10^{-3}$ M. Supporting electrolyte is $LiClO_4$. Specific rates are averages of two to five replicate runs; agreement between runs was better than 6%. [b] $\mu = 4.0$. [c] Experiments by Mrs. Jean Thomas. [d] Slight autocatalysis.

have been correlated by linear free energy relationships[24] are the reductions by Cr^{2+}, V^{2+}, and Eu^{2+} of a number of $(NH_3)_5Co^{III}$ derivatives in which the ligands do not partake in bridging.[3d,8] Although in a single case[3d] such a correlation has been applied to a series in which the bridging ligand is varied, it is anticipated that general applicability to inner-sphere reactions would be limited, and failure would be expected when rates are enhanced by chelating substituents or additional conjugated lead-in sites, for these are known to exhibit selectivity of action toward the various reducing metal ions.

The eleven alicyclic complexes initially listed in Table II are free from such complicating features, and here the pattern of rates for Eu^{2+} closely follows that for Cr^{2+}. A log-log plot of k values for the two reductants (Figure 1) is very nearly linear, with the least-squares line corresponding to the equation $\log k_{Eu} = 0.67 \log k_{Cr} + 0.54$. The slope is significantly less than 1.0, the value observed for the corresponding outer-sphere reductions[8] and predicted for the latter by Marcus.[20] As with the V^{2+}-Cr^{2+} correlation,[3d] the parallelism indicates, but does not prove, a similarity in mechanism for the two reductants. The importance of nonbonded interactions between the side chain and the reducing center within carboxylato series has been noted,[3d,11b] and values of $\log k_{Eu}$ within this group are related also to Taft's steric substituent parameters (E_s values).[25] The scatter in the Taft plot (Figure 2) is surprisingly slight (correlation coefficient 0.986) in view especially of the circumstance that E_s values are obtained primarily from rates of hydrolysis of esters (in which the carbonyl carbon suffers attack), whereas in the present series of reductions, attack may be presumed to occur at the carbonyl oxygen.[26] The quality of fit is, however, doubtless improved by our omission of the formato complex (for which recent evidence, based on nuclear Overhauser studies,[27] indicates conformational enhancement of inner-sphere rates unique to this complex), and α-fluoro-substituted complexes, for which specific neighboring group effects (*vide infra*) may come into play. Note that the formato value falls very close to the Eu^{2+}-Cr^{2+} line (Figure 1), as does the very high specific rate for the pyruvato complex III. Thus, the implication here is that any peculiarities of the activation profile associated with these ligands are comparably important for the reducing centers. The benzoato derivative is seen also to conform to the indicated pattern, and, as in the case of the Cr^{2+} reductions,[11a] incorporation of neither electron-attracting nor electron-donating ring substituents alters reduction rates substantially.

Rate Enhancement by Neighboring Groups. One of the distinguishing features of inner-sphere reduction paths is acceleration by neighboring donor groups in positions permitting chelation. In a number of Cr^{2+} reductions[11a,28] and in one by V^{2+},[3b] evidence has been presented that the initial Cr(III) or V(III) product is a chelate, thus implying chelation in the transition state; but characterization of the primary oxidation product from a Eu^{2+} reaction, which yields a substitution-labile Eu^{III} species, almost certainly requires time resolution which our present methods cannot provide. Note, however, that of the 19 complexes in Tables II and III exhibiting $k_{Eu^{2+}}$ values greater than 2 M^{-1} sec^{-1}, all but three have donor centers lying α, β, or γ to the coordinated carboxyl. The high Eu^{2+} rates for the oxalato, pyruvato (III), and thiodiglycolato (XVI) complexes bring to mind comparable accelerations induced by these ligands in the Cr^{2+} series, but values for the glycolato and lactato (I) derivatives indicate that Eu^{2+} reductions are considerably more responsive than Cr^{2+} or Cu^+ reductions to incorporation of an α-OH group. A similar inference may be drawn concerning α-alkoxy substitution from the unexpectedly high $k_{Eu^{2+}}$ values for the *O*-benzylglycolato and oxydiacetato (II) complexes. On the other hand, rate enhancement associated with α-mercapto substituents[4b,11b] in reductions by Cr^{2+} and Cu^+ (as seen, for example, in the reactions of oxidant VI) does not extend to Eu^{2+} reductions. This reversal of sensitivity in going from O donors to S donors adds to earlier evidence[4b] that neighboring group acceleration of electron-transfer reactions is most pronounced when the reducing metal center and the donor site are complementary in the Pearson sense,[9] and this view is bolstered by the enhancement of $k_{Eu^{2+}}$ resulting from attachment of a single fluoro to the acetato complex and more forcefully by the 20-fold acceleration upon incorporation of an α-SO_3^- group.[29] Neither of these very "hard" donor substituents accelerates reductions by Cr^{2+} or Cu^+.[30]

The very high rates for the pyruvato (III) and related benzoylformato (IV) derivatives warrant comment, for

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[24] (a) P. R. Wells, "Linear Free Energy Relationships," Academic Press, London, 1968; (b) D. P. Rillema, J. F. Endicott, and R. C. Patel, *J. Amer. Chem. Soc.*, **94**, 394 (1972).

[25] R. W. Taft, Jr., "Steric Effects in Organic Chemistry," M. S. Newman, Ed., Wiley, New York, N. Y., 1956, p 598.

[26] K. L. Scott and A. G. Sykes, *J. Chem. Soc., Dalton Trans.*, 1832 (1972).

[27] R. J. Balahura and R. B. Jordan, *Inorg. Chem.*, **12**, 1438 (1973).

[28] (a) R. D. Butler and H. Taube, *J. Amer. Chem. Soc.*, **87**, 5597 (1965); (b) A. Liang and E. S. Gould, *ibid.*, **92**, 6791 (1970); (c) M. V. Olson and H. Taube, *Inorg. Chem.*, **9**, 2072 (1970).

[29] A specific rate (25°, $\mu = 1.0$) of 30 M^{-1} sec^{-1} has been obtained for the Eu(II) reduction of the $(NH_3)_5Co^{III}$ complex of sulfoacetic acid in preliminary experiments by P. K. Thamburaj, Kent State University, 1973. The rate of this reduction does not appear to be acid dependent.

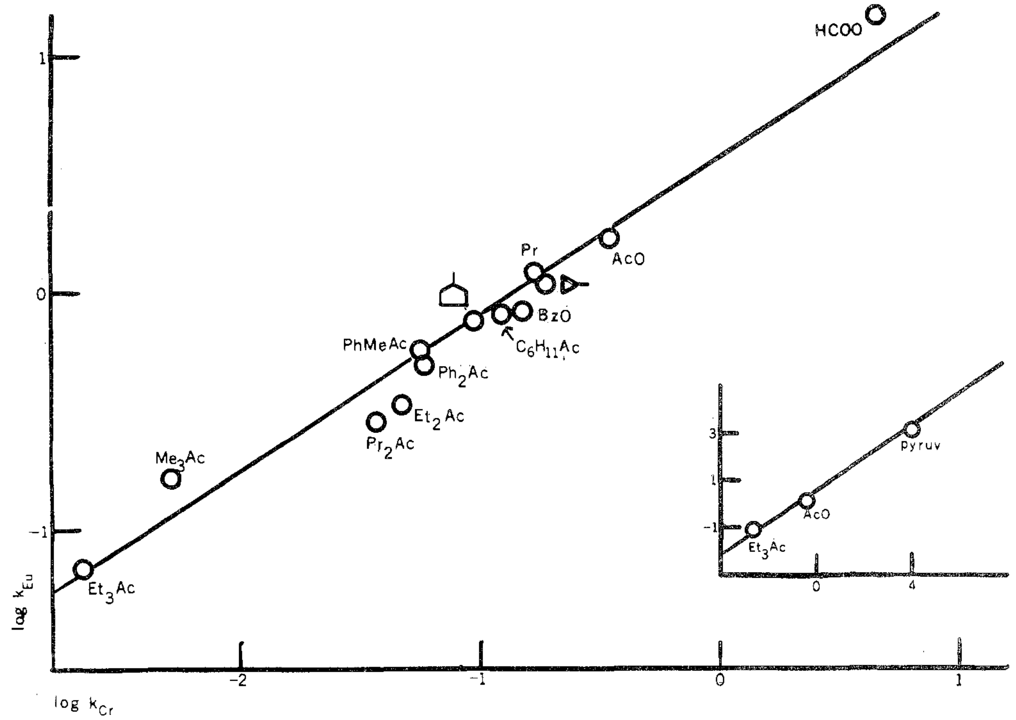

Figure 1. log-log plot comparing the specific rates of reductions of carboxylatopentaamminecobalt(III) complexes $R(NH_3)_5Co^{2+}$ by Eu^{2+} and Cr^{2+} [rate constants at 25° and $\mu = 1.0$; Pr = propionato, $C_6H_{11}Ac$ = cyclohexylacetato, pyruv = pyruvato (III)]. The least-squares line shown corresponds to the equation $\log k_{Eu} = 0.67 \log k_{Cr} + 0.54$ with a correlation coefficient of 0.989.

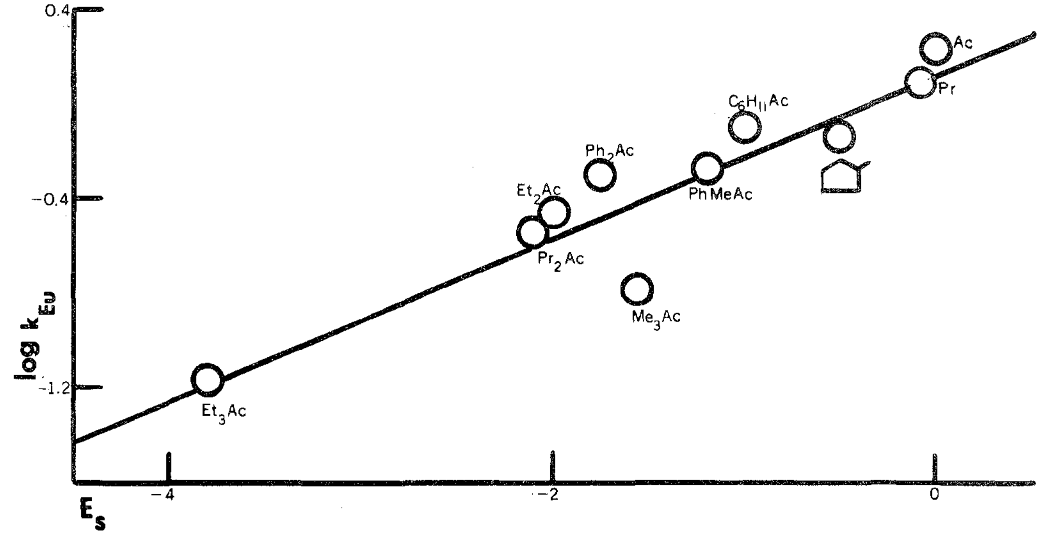

Figure 2. Correlation of specific rates of reduction, using Eu^{2+}, of carboxylatopentaamminecobalt(III) complexes $(NH_3)_5RCOOCo^{2+}$ with Taft's steric substituent parameters (E_s values).[25] [Rate constants refer to reactions at 25° and $\mu = 1.0$; Pr = propionato, $C_6H_{11}Ac$ = cyclohexylacetato.] The least-squares line shown corresponds to the equation $\log k_{Eu} = 0.35E_s + 0.13$. The correlation coefficient is 0.986.

recent evidence[3a,17b] argues strongly against intervention of a chelated transition state and therefore against electron transfer through the neighboring carbonyl group, in reductions of complexes of this sort. The similarity in kinetic response by Cr^{2+} and Eu^{2+} (note the pyruvato point in Figure 1) is in keeping with the suggestion that acceleration in such instances reflects conjugative stabilization of a radical-cation transition state lying between the binuclear precursor and the successor complex,[17b] for the operation of such stabilization should depend primarily on the potential of the reducing species, and selective coordinating effects associated with the metal centers should play no role here. In accord with this view, rate enhancement by the pyruvato ligand is slight with Ti^{3+},[31,32] which is less strongly reducing than either Cr^{2+} or Eu^{2+}, and marginal with Cu^+.[4b]

Acidity Patterns. The (H^+) dependencies observed for the Eu(II) reductions in Table III closely resemble those described for the corresponding reactions of Cr(II)[2c] and thus con-

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(30) The most striking mediating effects in the Cr^{2+} and Cu^+ series are associated with nearby heterocyclic (pyridine and pyrazine) nitrogen centers. Although comparisons with Eu^{2+} are complicated by the frequent occurrence of strong autocatalysis in such systems, it appears that rate enhancement by neighboring nitrogen extends also to this reductant, although perhaps with attenuation. Our data for reduction of the 2-pyridinecarboxylato complex, which is but slightly autocatalytic, fit the equation rate = $[Eu^{II}][Co^{III}](2.1 + 0.06/[H^+])$. The coefficient of the inverse-acid term, in conjunction with the estimated pK_A of 4.0 for the protonated form of the oxidant,[4b] yields a specific rate $6 \times 10^2\ M^{-1}\ sec^{-1}$ for reduction of this complex in its basic form, approximately 3 powers of 10 below the corresponding value for Cr^{2+}. A similar comparison for the rapidly reacting 2,6-pyridinedicarboxylato complex is not possible, for $k_{Eu^{2+}}$ is acid independent, whereas $k_{Cr^{2+}}$ is very nearly inverse acid.[17b]

Table IV. Acid-Accelerated Reductions of Carboxylatopentaamminecobalt(III) Complexes[a]

Organic ligand	$k_{\mathrm{Cr}^{2+}}$	$k_{\mathrm{Eu}^{2+}}$	$k_{\mathrm{V}^{2+}}$
p-Formylbenzoato (XIII)	$53 + 3.8 \times 10^2(\mathrm{H}^+)$[b]	$1.08 + 0.31(\mathrm{H}^+)$[b] $1.20 + 0.18(\mathrm{H}^+)$[c,d]	$0.88 + 0.24(\mathrm{H}^+)$[b] $2.21 + 0.66(\mathrm{H}^+)$[d,e]
p-Benzoylbenzoato	$0.32 + 1.5(\mathrm{H}^+)$[f]		
p-Formylcinnamato (XIV)	$260 + 1.8 \times 10^3(\mathrm{H}^+)$[g]	$4.2 + 3.0(\mathrm{H}^+)$[c]	
Mucochlorato (XV)		$80 + 6.1 \times 10^2(\mathrm{H}^+)$[c]	

[a] Specific rates in M^{-1} sec^{-1} at 25°; $\mu = 1.0$ unless otherwise indicated. [b] Reference 10b. [c] This work. [d] $\mu = 4.0$. [e] Reference 3d. [f] Reference 11a; $\mu = 3.0$. [g] Reference 17b; $\mu = 1.2$.

stitute additional evidence that the two reducing centers utilize a common set of mechanisms. The most straightforward interpretation of such variation with acidity, the coexistence of a protonated and deprotonated form of the oxidant, in mobile equilibrium but reduced at different specific rates, leads to the rate law[17a,28b]

$$\text{rate} = [\mathrm{Eu^{II}}][\mathrm{Co^{III}}]\frac{kK_\mathrm{A} + k'[\mathrm{H}^+]}{K_\mathrm{A} + [\mathrm{H}^+]} \tag{1}$$

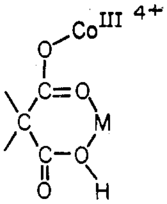
where specific rates k and k' refer to the deprotonated and protonated forms and K_A is the acidity constant for the oxidant.

The present acetato data, in combination with the recorded value of K_A for this complex (0.44 M at $\mu = 4.0$),[17a,19] yield specific reduction rates of 2.36 M^{-1} sec^{-1} for the familiar nonprotonated form and 0.25 for the protonated form.[33] We cannot be certain as to whether the latter reaction component represents an inner- or outer-sphere reduction.[34] With Cr^{2+} as a reductant, identification of products should allow a choice as to mechanism, but here the protonated acetato path has been reported to be undetectably slow.[17a] Although the specific rate for outer-sphere reduction of the nonprotonated acetato complex by Eu(II) is estimated as only 0.003 M^{-1} sec^{-1},[35] indications that outer-sphere rates in this series are strongly enhanced by electron withdrawal from the coordination site[35] lead us to favor an outer-sphere path for the protonated component.

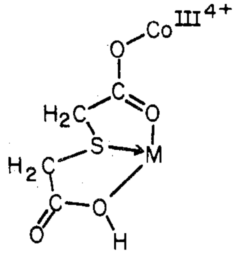
The reductions, by Cr^{2+}, of five of the derivatives in Table II occur, in part, by inverse-acid paths; each of these oxidants features an acidic center lying near the coordinated carboxyl, as do many additional Co(III) complexes[11a,28b] exhibiting similar behavior.

Here again we are doubtless dealing with a chelated transition state from which the carboxyl hydrogen has been lost. The erosion, in the Eu^{2+} series, of this path is unexpected, for it would seem that chelation of the very "hard" carboxylato group during reduction should give the kinetic advantage to the lanthanide center. We conclude, therefore, that substitution of Eu^{2+} for Cr^{2+} sharply lowers the acidity of a protonated precursor (*e.g.*, XIX) and, in that way, diminishes the importance of the deprotonated path.

Only with three of the oxidants does the $(\mathrm{H}^+)^{-1}$ path survive for Eu^{2+} (Table III). With the 2-pyridinecarboxylato complex, this contribution is marginal, whereas with the oxalato complex, it may be related to the ease with which the reducing center coordinates with this very strongly chelating ligand.[36] Data for the thiodiglycolato complex (XVI) lead to a specific rate of $15 + 0.33/(\mathrm{H}^+)$ M^{-1} sec^{-1}, while the glutarato complex, in which $-\mathrm{CH}_2-$ replaces the donor sulfur, but which is otherwise structurally similar, is reduced at the "normal" rate and without acid dependency. The contrast here suggests the doubly chelated precursor complex XX for the acid-independent component in the reduction of XVI and its conjugate base for the inverse-acid portion.[37]



XIX



XX

$\mathrm{M} = \mathrm{Cr}^{2+}, \mathrm{Eu}^{2+}$

Three of the complexes in the present study react more rapidly at high acidities than at low (Table III), and in each case the specific rates conform to an expression of the type $k_0 + k_{\mathrm{HA}}[\mathrm{H}^+]$ (Table IV). For the *p*-formylbenzoato

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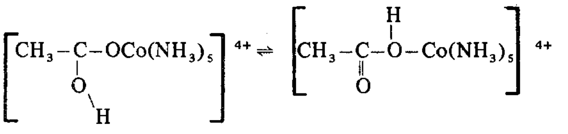
(31) Measurements in 1.0 M *p*-toluenesulfonic acid (A. H. Martin and E. S. Gould, Kent State University, 1972) yield a specific rate of 0.4 M^{-1} sec^{-1} for Ti^{3+} reduction of the pyruvato complex in this series (III) and 0.02 M^{-1} sec^{-1} for the corresponding reduction of the formato. In related experiments, addition of a deficiency of Cr^{2+} to the benzoylformato complex (IV) is found to result in the very rapid formation of a strongly absorbing ($\lambda_{\max}$ 640 nm, $\epsilon > 10^3$) intermediate which slowly decays with release of Co(II). The behavior here, which is remarkably similar to that observed during Cr^{2+} reduction of the pyrazinecarboxylato complex,[32] suggests the intervention of a radical species bound to both Co(III) and Cr(III).

(32) E. S. Gould, *J. Amer. Chem. Soc.*, 94, 4360 (1972).

(33) These specific rates may be conveniently obtained by plotting the function $k_{\mathrm{obsd}}(K_\mathrm{A} + [\mathrm{H}^+])$ against $[\mathrm{H}^+]$. The slope of the resulting least-squares fit is k'; the intercept, kK_A.

(34) In view of evidence[26] that inner-sphere reduction of carboxylato complexes involves attack at the carbonyl oxygen, an inner-sphere mechanism for reduction of the protonated acetato complex is admissible only if the oxidant is a mixture of tautomers XVII and XVIII with a substantial fraction of the latter.



$$\left[\mathrm{CH_3{-}\underset{\underset{\textstyle\diagdown_{H}}{O}}{\overset{|}{C}}{-}OCo(NH_3)_5}\right]^{4+} \rightleftharpoons \left[\mathrm{CH_3{-}\underset{O}{\overset{\|}{C}}{-}\overset{\overset{H}{|}}{O}{-}Co(NH_3)_5}\right]^{4+}$$

XVII XVIII

(35) Outer-sphere reductions of Co(III) complexes by $\mathrm{Ru(NH_3)_6}^{2+}$ have been found to be about 8 times as rapid as those by Eu(II).[16] The acetato and trifluoroacetato complexes are reduced by $\mathrm{Ru(NH_3)_6}^{2+}$ at specific rates 0.022 and 0.18 M^{-1} sec^{-1}.

(36) A. Glasner, E. Levy, M. Steinberg, and W. Bodenheimer, *Talanta*, 11, 405 (1964).

(37) We attach no fundamental significance to the apparent absence of an inverse-acid path in the very rapid Eu(II) reduction of the oxydiacetato complex, II. If such a path were to have a specific rate comparable to that for its sulfur analog, XVI, it would constitute only about 6% of the total reaction at the lowest acidity studied, and hence could be overlooked. It would presumably be detectable at much lower acidities where, however, reliable rate measurements are much more difficult.[28b] Of greater concern is the lack of acid dependence in the reductions of the α,β-unsaturated complexes IX and X, for dependencies observed in the Cr^{2+} series have earlier been interpreted[19] as indications that these complexes exist as mixtures of protonated and nonprotonated forms reduced at significantly different specific rates. It now appears that the Cr^{2+} trends, which have been noted by at least three observers, may reflect medium effects of unusual intensity. Why such effects should be peculiar to this reducing center and this type of unsaturated oxidant remains a puzzling point.

derivative (XIII), we find the first-order acid path at $\mu = 4.0$ to be marginal, in agreement with the work of Zanella and Taube at much lower ionicity,[10b] whereas with the *p*-formylcinnamato (XIV) and mucochlorato (XV) complexes, this path is a major kinetic component. In reductions with Cr^{2+},[2c] Cu^{+},[4b] and V^{2+},[3d] the [H^{+}]^{1} term is observed only when an unsaturated lead-in group lies remote from, but in conjugation with, COOCo^{III}. Kinetic behavior of this sort is thought to be diagnostic of electron transfer through an extended portion of the ligand (in both paths[10b]), and in two cases involving Cr^{2+},[10b,17b] an intermediate having Cr(III) bound to the remote lead-in atom has been detected. The extension of this type of rate law, with appropriately substituted oxidants, to the Eu^{2+} series indicates that this metal center may partake in still another known variant of the inner-sphere mechanism.

For the two of the oxidants in Table IV where the Eu^{2+} rates may be compared with those of Cr^{2+}, the latter enjoys a striking kinetic advantage in both kinetic components, in marked contrast to the slower carboxylato complexes which react more rapidly with Eu^{2+}. Although perhaps not predicted, this reversal is in keeping with alterations in the lead-in substituent and the electron-transfer path associated with incorporation of the remote carbonyl group. Moreover, when the lead-in site is further softened by replacing C=O with C=N and possible chelating functions are withheld, evidence for a remote path involving Eu^{2+} disappears.[8]

In summary, the present results, when taken in concert, point strongly to the importance of several variants of the inner-sphere path in reductions by Eu^{2+}, but the picture is thus far largely qualitative. For all reactions considered, an outer-sphere component exists, but how the magnitude of this component depends on the structure of the mediating ligand, whether it changes significantly when Eu^{2+} is replaced with other reducing centers, and under what circumstances it becomes predominant are questions that remain unanswered. It is these matters to which we shall turn our attention in a companion paper.[38]

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Registry No. Eu^{2+}, 16910-54-6; Cr^{2+}, 22541-79-3; triethylacetatopentaamminecobalt(III), 51965-36-7; trimethylacetatopentaamminecobalt(III), 33887-25-1; di-*n*-propylacetatopentaamminecobalt(III), 51965-52-7; diethylacetatopentaamminecobalt(III), 51965-53-8; diphenylacetatopentaamminecobalt(III), 47197-62-6; phenylmethylacetatopentaamminecobalt(III), 34371-95-4; cyclopentanecarboxylatopentaamminecobalt(III), 51965-54-9; cyclohexylacetatopentaamminecobalt(III), 51965-55-0; cyclopropanecarboxylatopentaamminecobalt(III), 46057-30-1; propionatopentaamminecobalt(III), 19173-62-7; formatopentaamminecobalt(III), 19173-64-9; glycolatopentaamminecobalt(III), 31279-86-4; lactatopentaamminecobalt(III), 34464-03-4; *o*-benzylglycolatopentaamminecobalt(III), 51965-56-1; oxydiacetatopentaamminecobalt(III), 45160-35-8; pyruvatopentaamminecobalt(III), 19306-91-3; benzoylformatopentaamminecobalt(III), 49861-82-7; furoatopentaamminecobalt(III), 51965-57-2; acetoxyacetatopentaamminecobalt(III), 45124-43-4; fluoroacetatopentaamminecobalt(III), 51965-33-4; difluoroacetatopentaamminecobalt(III), 51965-58-3; trifluoroacetatopentaamminecobalt(III), 19173-66-1; trichloroacetatopentaamminecobalt(III), 19998-53-9; *S*-benzylthioglycolatopentaamminecobalt(III), 46923-07-3; *Se*-benzylselenoglycolatopentaamminecobalt(III), 51965-37-8; *β*-benzylmercaptopropionatopentaamminecobalt(III), 51965-38-9; malonatopentaamminecobalt(III), 38897-90-4; 1,1-cyclobutanedicarboxylatopentaamminecobalt(III), 50578-38-6; succinatopentaamminecobalt(III), 51965-39-0; glutaratopentaamminecobalt(III), 51965-40-3; maleatopentaamminecobalt(III), 17712-86-6; benzoatopentaamminecobalt(III), 30931-77-2; *p*-hydroxybenzoatopentaamminecobalt(III), 30931-75-0; salicylatopentaamminecobalt(III), 30931-74-9; *o*-acetylbenzoatopentaamminecobalt(III), 51965-41-4; *o*-thiomethylbenzoatopentaamminecobalt(III), 51965-42-5; *o*-formylbenzoatopentaamminecobalt(III), 42532-71-8; terephthalatopentaamminecobalt(III), 50578-83-1; *p*-hydroxycinnamatopentaamminecobalt(III), 46922-32-1; *o*-hydroxycinnamatopentaamminecobalt(III), 46913-88-6; furanacrylatopentaamminecobalt(III), 52021-51-9; 3-pyridinecarboxylatopentaamminecobalt(III), 52021-52-0; *N*-methyl-2-pyridinecarboxylatopentaamminecobalt(III), 52021-53-1; 2,6-pyridinedicarboxylatopentaamminecobalt(III), 46913-60-4; pyrazinecarboxylatopentaamminecobalt(III), 37112-48-4; *p*-formylbenzoatopentaamminecobalt(III), 19743-65-8; *p*-formylcinnamatopentaamminecobalt(III), 51965-34-5; mucochloratopentaamminecobalt(III), 51965-35-6; oxalatopentaamminecobalt(III), 19306-87-7; thiodiglycolatopentaamminecobalt(III), 51965-32-3; 2-pyridinecarboxylatopentaamminecobalt(III), 46422-51-9; carbonatopentaamminecobalt(III) chloride, 13682-58-1.

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