of Φ_{py} (μ = 2.0 *M*) with two principal differences. At the lower ionic strength, the lowest pH possible was insufficient to attain a Φ_{py} plateau, and the acid-dependent pathway begins to take effect at a lower pH. The latter observation, a shift of the Φ_{py} *vs.* pH curve to the left, indicates a decreased sensitivity of the system to H^+ concentration. Regardless of the actual mechanism, the observation of decreased sensitivity to H^+ at lower ionic strength is consistent with the supposition that the pH dependence of Φ_{py} reflects the reaction of H^+ with another cationic species,[31] *e.g.*, A or CT_2*.

Other $Ru(NH_3)_5L^{2+}$ Complexes. The most striking features of the Φ_L values obtained for the complexes $Ru(NH_3)_5L^{2+}$ (Figure 2) is the pH insensitivity for L = benzonitrile and for L = 3-chloropyridine and the similarity of the data obtained for the 4-methylpyridine complex to that for the pyridine complex. Only in 2 *M* HCl does the 3-chloropyridine show a small enhancement (20–30%) of Φ_L while, within experimental uncertainty, Φ_L is unchanged for the benzonitrile complex. These observations are consistent with a step in the mechanism involving protonation of the ligand nitrogen atom. Benzonitrile, a very weak Brønsted base,[32] should be less susceptible to a protonation pathway as should 3-chloropyridine (pK_a = 2.8),[24] a weaker base than pyridine (pK_a = 5.3). As a result, the Φ_L *vs.* pH curve for the 3-chloropyridine complex should be shifted to lower pH while, in contrast, the complex of 4-methylpyridine (pK_a = 6.1)[24] should participate as well as the pyridine analog in a competitive acid-dependent step. These predictions are consistent with the data (Figures 1 and 2). Another interesting observation for the various pyridine complexes can be drawn from comparing values at which the quantum yields plateau in the higher pH range. These values follow the order ($\Phi_{(3\text{-chloropyridine})} > \Phi_{(\text{pyridine})} > \Phi_{(4\text{-methylpyridine})}$). This, incidentally, is opposite to that observed for the second-order rate constants [*k*(4-methylpyridine) > *k*(pyridine) > *k*(3-chloropyridine)] measured[24] for the thermal reaction of $Ru(NH_3)_5H_2O^{2+}$ with the various ligands to form the respective $Ru(NH_3)_5L^{2+}$ ions.

Acknowledgments. This work was supported by the National Science Foundation (GP-26199), the Research Corporation, and the Petroleum Research Fund, administered by the American Chemical Society (4023-A3). We are indebted to Professors R. J. Watts and Henry Offen of University of California, Santa Barbara, for helpful discussion and the latter for the loan of certain equipment. The mass spectrometer used in the H/D exchange experiments was purchased with the help of the National Science Foundation (NSF-GP-8593).

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(31) R. P. Bell, "Acid-Base Catalysis," Oxford University Press, London, 1941, p 32.

(32) L. P. Hammett and A. J. Deyrup, *J. Amer. Chem. Soc.*, **54**, 4239 (1932).

Electron Transfer through Organic Structural Units. XI. Reductions of Pentaamminecobalt(III) Derivatives of Heterocyclic Bases with Chromium(II) and Europium(II)[1a]

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Abstract: The reductions, with Eu^{2+}, of 20 heterocyclic pentaamminecobalt(III) complexes, nine of them new, are compared to the corresponding Cr^{2+} reductions. In most cases the ratio of specific rates, $k_{Eu^{2+}}/k_{Cr^{2+}}$ (25°, μ = 1.3), lies in the range 8–25. Deviations from this pattern occur only with ligands having sites allowing reduction *via* remote attack; among such ligands are 4-carbethoxypyridine, methylated pyrazines, and 4-pyridone. In such instances, reduction with Cr^{2+} is strongly enhanced, but rate increases with Eu^{2+} are very slight. Spectra of solutions resulting from Cr^{2+} reduction of the pyrazine complexes indicate that the Cr(III) products are N-bonded to the pyrazine ring. Inner-sphere reduction by Eu^{2+}, if it occurs at all, is marginal in magnitude. The Cr^{2+} and Eu^{2+} reductions of the complex of *trans*-1,2-bis(4-pyridyl)ethylene (II) and the Eu^{2+} reduction of the 4-carbethoxypyridine derivative exhibit strong autocatalysis, suggesting intervention of an unusually reactive radical or radical cation. When $(NH_3)_5pyCo^{3+}$ is added to mixtures in which such autocatalytic reactions are occurring, it too is rapidly reduced. The suggestion is made that such reactive species operate through outer-sphere mechanisms.

The richness of the reactivity patterns observed in the Cr^{2+} reductions of organic $(NH_3)_5Co^{III}$ derivatives[2] has not yet been encountered with any other reducing center. Reductions with Cu^+, which is less strongly reducing than Cr^{2+} by 0.56 V, exhibit signs of the same mechanistic variations that come into play with Cr^{2+}, but the trends are less intense.[3] Moreover, rates of reductions with the still more poorly reducing Fe(II) are gathered at the very slow end of the kinetic scale.[4] On the other hand, reductions by the strongly

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(1) (a) From the Ph.D. Dissertation of E. R. Dockal, Kent State University, 1971. This work was supported in part by the Petroleum Research Fund, administered by the American Chemical Society, under Grant 2878-A3. (b) NSF Trainee, 1969–1971.

(2) See, for example, H. Taube and E. S. Gould, *Accounts Chem. Res.*, **2**, 321 (1969).

(3) (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).

(4) See, for example, J. H. Espenson, *Inorg. Chem.*, **4**, 121 (1965).

Table I. Pentaamminecobalt(III) Perchlorates, $RCo(NH_3)_5(ClO_4)_3$

R	Solvent	Heating time, min (°C)	Calcd, % C	Calcd, % H	Calcd, % Co	Found, % C	Found, % H	Found, % Co[b]	ϵ_{475}[a]
4-Phenylpyridine	DMF	5 (100)	22.1	4.05	9.9	22.2	4.13	9.9	53
Isoquinoline (I)	S[c] or TEP	180 (50)	18.9	3.88	10.3	18.7	4.08	9.9	72
3-Ethylpyridine	DMF	10 (90)	15.3	4.40	10.8	14.6	4.38	10.6	61[d]
3-Carbomethoxypyridine	DMF	120 (90)	14.5	3.83	10.2	14.8	3.70	9.9	65
4-Carbethoxypyridine	S or TEP	180 (50)	16.2	4.08	9.9	16.1	4.01	9.6	66[d]
1,2-Bis(4-pyridyl)ethylene (II)[e]	DMF	10 (100)	23.0	4.03	9.4	22.0	4.33	9.1	82
1,2-Bis(4-pyridyl)ethane	DMF	10 (100)	23.0	4.34	9.4	22.8	4.27	9.1	68
2-Methylpyrazine	DMF	30 (100)	11.2	3.95	11.0	11.3	3.98	10.7	72[d]
2,6-Dimethylpyrazine (III)	DMF	30 (100)	13.1	4.21	10.7	12.9	4.38	10.6	71[d]

[a] λ_{max} at 475 nm for all complexes. [b] See ref 9. [c] Sulfolane. [d] Shoulder at 330 nm. [e] For evidence that this ligand is a trans olefin, see T. Katsumoto, *Bull. Chem. Soc. Jap.*, **33**, 1376 (1960).

reducing cations, U^{3+} and Yb^{2+}, are so rapid[5] that kinetic features which might otherwise diagnose mechanistic differences are blurred, whereas rates of inner-sphere reductions by V^{2+} appear to be limited by rates of ligand substitution about V(II).[6]

It is, at present, not clear how important inner-sphere paths are in reduction with Eu^{2+}. Substantial variations in the specific rates of reduction of the halogenopentaamminecobalt(III) complexes suggest a transition state having a halogen bridge,[7a] but no strong support for bridging emerges from the study of reductions of the corresponding carboxylatocobalt(III) complexes.[7b] The present study compares the rates of reduction, with Cr^{2+} and Eu^{2+}, of a number of N-coordinated heterocyclic pentaamminecobalt(III) derivatives. This type of oxidant was chosen because mechanistic variations are, in favorable instances, more vividly reflected in rate differences than is the case for the more easily prepared carboxylato complexes.[8] We find no strong evidence of inner-sphere reduction by Eu^{2+} in this series. Both outer- and inner-sphere mechanisms appear to operate for reductions by Cr^{2+}, which, in addition, exhibit some elements of novelty.

Experimental Section

Materials. Aquopentaamminecobalt(III) perchlorate,[9] azidopentaaminecobalt(III) perchlorate,[10] and nitrosyl perchlorate[11] were prepared as described. Heterocyclic ligands (Aldrich products) were distilled if discolored and dried over Linde activated molecular sieves (Type 3A or 4A). Triethyl phosphate and sulfolane were vacuum distilled under nitrogen; the former was stored over molecular sieves, the latter over calcium hydride. Lithium perchlorate, for kinetics experiments, was prepared by neutralizing reagent grade lithium carbonate with perchloric acid and was twice recrystallized from water before being used. Chromium(II) perchlorate solutions were prepared and analyzed as described.[9]

Europium(III) perchlorate was prepared in solution by dissolving Eu_2O_3 (Alfa Inorganics, Inc.) in perchloric acid and then filtered to remove unreactive solid. Europium(II) perchlorate solutions were prepared by reduction of a master solution of Eu(III) with zinc amalgam and were stored over this amalgam in a vial stoppered with a rubber serum cap. The concentration of Eu(II) was determined by adding a known volume of the solution to excess chloropentaamminecobalt(III) perchlorate[9] under nitrogen, diluting tenfold with concentrated HCl, and reading the absorbance at 692 nm of the $CoCl_4^{2-}$ formed (ϵ = 560).[12] Eu(II) solutions were used within 8 hr of their preparation to minimize reduction of ClO_4^-.

Preparation of the Complexes. A number of the heterocyclic complexes needed were available from previous studies[8a] or could be prepared, without substantial modification of literature procedures,[8a,13] from the aquopentaammine perchlorate and the free ligand in dimethylformamide. Heating times and conversion temperatures are listed in Table I. For the complex of 1,2-bis(4-pyridyl)ethylene, the general procedure was slightly modified. A mixture of 1.5 ml of DMF and 1.0 g of the aquo complex was heated, with stirring, at 90° for 15 min. The free ligand (2.0 g) was then added and stirring continued at 90° for 10 min more. The orange-red solution was cooled and extracted with several 100-ml portions of ether. The remaining oil was dissolved in 15 ml of methanol and the solution filtered to remove the unreacted aquo- and DMF-substituted perchlorates. To the methanolic solution was added 4-6 ml of saturated methanolic sodium iodide, and the solution was allowed to cool at −10° for 2 hr. The yellow solid which precipitated was filtered off and washed with ethanol and then with ether. It was immediately dissolved in a minimum volume of water at 60°, and the preparation filtered twice to remove unreacted ligand. The filtrate, a solution of the complex iodide, was cooled, allowing the solid iodide to crystallize. The iodide was converted to the corresponding perchlorate by dissolving in water, adding an equal volume of saturated aqueous sodium perchlorate, and then cooling to −10°.[14] The complex perchlorate was recrystallized from water.

In cases where no appreciable conversion to the heterocyclic complex occurred in DMF, a more severe method, in which the azidopentaammine perchlorate was treated with $NOClO_4$, was attempted.[10b,13b] The azido complex (1.0 g) was dissolved in 5 ml of triethyl phosphate or dry sulfolane, and a slight excess (10-20%) of dry nitrosyl perchlorate was added. The mixture was allowed to stand until evolution of N_2 and N_2O ceased and the solution turned from reddish violet to rose red. Excess nitrosyl perchlorate was destroyed by heating at 30°, with stirring, for 30 min. After addition of 5 ml of the organic ligand, the mixture was heated with stirring; times and temperatures are listed in Table I. The rose color of the solution changes to red-orange when reaction is complete. The preparation was then extracted with several portions of ether, the oil dissolved in 15 ml of methanol, the preparation filtered, and the residue discarded. Precipitation of the complex iodide and conversion to the perchlorate were carried out as in the preparation in DMF. For this method, both the solvent and the ligand were

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[5] (a) R. T. Wang and J. H. Espenson, *J. Amer. Chem. Soc.*, **93**, 380 (1971); (b) R. J. Christensen and J. H. Espenson, *Chem. Commun.*, 756 (1970).

[6] (a) P. R. Guenther and R. G. Linck, *J. Amer. Chem. Soc.*, **91**, 3796 (1969); (b) C. Norris and F. R. Nordmeyer, *Inorg. Chem.*, **10**, 1235 (1971).

[7] (a) J. P. Candlin, J. Halpern, and D. L. Trimm, *J. Amer. Chem. Soc.*, **86**, 1019 (1964); (b) R. T. M. Fraser, *ibid.*, **84**, 3436 (1962).

[8] (a) E S. Gould, *ibid.*, **89**, 5792 (1967); (b) F. Nordmeyer and H. Taube, *ibid.*, **90**, 1162 (1968).

[9] E. S. Gould and H. Taube, *ibid.*, **86**, 1318 (1964).

[10] (a) M. Linhard and H. Flygare, *Z. Anorg. Allg. Chem.*, **262**, 328 (1950); (b) R. B. Jordan, A. M. Sargeson, and H. Taube, *Inorg. Chem.*, **5**, 1091 (1966).

[11] G. Brauer, "Handbook of Preparative Inorganic Chemistry," English ed, Vol. 1, Academic Press, New York, N. Y., 1965, p 320.

[12] E. S. Gould, *J. Amer. Chem. Soc.*, **88**, 2983 (1966).

[13] (a) E. S. Gould, *ibid.*, **87**, 4730 (1965); (b) Y. Wang and E. S. Gould, *ibid.*, **91**, 4998 (1969).

[14] Virtually all heterocyclic iodides encountered in this study are photosensitive. Dry samples darken quickly when exposed to light. In recrystallizing such iodides, care must be taken to minimize thermal decompositions; preparations should not remain above 60° for more than a few minutes. The perchlorates, in contrast to the iodides, appear to be stable at room temperature in the light for at least several weeks.

Table II. Chromium(III) Products Obtained from Chromium(II) Reductions of Pentaamminecobalt(III) Complexes, $RCo(NH_3)_5)^{3+}$

R	Cr(III) product	ϵ_1	λ_{max}, nm	ϵ_2	λ_{max}, nm
Aquo	$Cr(H_2O)_6^{3+}$	13.4	574	15.6	408
Pyridine[a]	$Cr(H_2O)_6^{3+}$				
3-Methylpyridine[b]		13.4	574	15.4	408
N,*N*-Dimethyl-3-carboxamidopyridine[c]	$Cr(H_2O)_6^{3+}$				
N,*N*-Dimethylformamide[c]	$Cr(H_2O)_6^{3+}$				
2-Pyridone (VI)[c]	$Cr(H_2O)_6^{3+}$				
4-Pyridone		25[d]	586	27	415
4-Carbethoxypyridine			570		408
2-Methylpyrazine		21.4	542	66	364
2,6-Dimethylpyrazine (III)		20.3	538	59	377

[a] See ref 8b. [b] See ref 13b. [c] See ref 22. [d] Principal product, formed in addition to $Cr(H_2O)_6^{3+}$ (see ref 22).

rigorously dried before use, and all operations prior to the ether extraction were carried out in a drybox under dry nitrogen. If moisture was present, the desired yellow heterocyclic complexes were seriously contaminated with the aquo complex, coloring them red or brown. The evolution of a brown gas on addition of $NOClO_4$ indicated that the system was not sufficiently dry. The quantity of $NOClO_4$ used should be carefully controlled. A 10–20% mol excess was best; smaller amounts left some of the azido complex unreacted, whereas a large excess resulted in one or more unwanted products. In several reactions with a large excess of $NOClO_4$, the isolated product (λ_{max} 460 nm) appeared to be nitropentaamminecobalt(III) perchlorate.[15]

Table I lists nine complexes which do not appear to have been described. Neither the general procedures above nor various modifications of these were successful in preparing $(NH_3)_5Co^{III}$ complexes of the following ligands: 2,6-dichloropyrazine, 3,5-dichloropyrazine, 2-vinylpyridine, 3-acetoxypyridine, benzimidazole, 1,2-bis(2-pyridyl)ethylene, 4-aminoacetophenone, 4-aminobenzophenone, 2,6-dimethylpyridine, 2-ethylpyridine, and 4-aminopyridine. Some conversion to the heterocyclic complex appeared to take place with 3-hydroxypyridine and 4-benzylpyridine, but pure products could not be isolated.

Kinetic Experiments. Rates were estimated from measurements of absorbance changes on the Cary 14 recording spectrophotometer, using the 0.0–0.2 absorbance unit slide wire.[8a] Measurements were generally carried out at 475 nm. All reactions were shown to be first order each in Co(III) and in reductant. Most rate measurements were made under pseudo-first-order conditions with at least a tenfold excess of reductant. Reductions were carried out in cylindrical cells fitted with rubber serum caps through which the reductant was added with a hypodermic syringe. A 1.0-cm cell was used for reactions having specific rates less than 2 M^{-1} sec^{-1} and a 10.0-cm cell for reactions with rate constants greater than this figure. For complexes having uncoordinated donor sites, rates were followed at three or more acidities in the range 0.25–1.2 M H^+. Ionic strengths were adjusted to near 1.3 M by the 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 7%; no trends indicative of systematic errors were noted, and average values did not differ significantly from values obtained from least-squares treatment of logarithmic plots of absorbance differences against reaction time. Specific rates obtained from different runs with the same pairs of reactants checked to better than 15%. Temperatures were kept at 25.0 ± 0.2° during the entire series of experiments.

Treatment of the complexes of 2-methyl- and 2,6-dimethylpyrazine with excess Cr^{2+} resulted in the rapid formation of an intensely absorbing green pigment,[13a] and the specific rates for reduction of Co(III) exceeded 100 M^{-1} sec^{-1}. Reactions were therefore followed by keeping the Co(III) complex (about 3 mg of the perchlorate) in excess and adding very small volumes of Cr^{2+}, using a graduated microsyringe.[16] The Eu(II) reductions of these pyrazine complexes were slower and did not yield any strongly absorbing material early in the reaction. Rates were therefore measured with excess Eu^{2+}. In a few cases, slight increases in absorbance were noted during the very late stages of the reaction; these were presumably due to slow reaction of excess Eu^{2+} with ligand released in the reduction. In such instances, specific rates were evaluated by the Guggenheim procedure,[17] and agreement between runs was within 10%.

The Eu^{2+} reduction of the 4-carbethoxypyridine complex and the Cr^{2+} and Eu^{2+} reductions of the 1,2-bis(4-pyridyl)ethylene complex did not follow, even in approximation, pseudo-first-order kinetics. Decreases in absorbance were linear, rather than logarithmic, during most of the reaction, finally "curving off" during the last few per cent.[18] Initial rates could be increased by addition of the uncomplexed ligand and were roughly proportional to its concentration. In separate experiments, $(NH_3)_5pyCo^{3+}(ClO_4^-)_3$ was added to reaction mixtures in which such autocatalytic reductions were taking place, whereupon it was reduced at rates 10–100 times as great as those observed in the ordinary kinetic runs. Similar accelerations resulted when the pyridine complex was reduced, using Cr^{2+} or Eu^{2+}, in the presence of the free ester or free ligand II.

Spectra of Cr(III) Products. Spectra of solutions resulting from a number of the faster Cr(II) reductions were taken; reaction mixtures contained 0.025 mequiv each of Co(III) and Cr(III) in 2.0 ml of 0.1 M $HClO_4$. Absorbancies of the chromium(III) products were obtained by subtraction of the absorbancy of Co^{2+}. The resulting spectra, augmented by the results of previous product studies from reactions of this kind, are summarized in Table II. Only with the complexes of 4-pyridone, 2-methylpyrazine, and 2,6-dimethylpyrazine was there evidence that the principal Cr(III) product was not $Cr(H_2O)_6^{3+}$.

Results and Discussion

Specific Rates. Comparison of Outer-Sphere Reductions by Cr(II) and Eu(II). Kinetic data are summarized in Table III. All reductions by Eu^{2+}, and all but one by Cr^{2+} in the present series, proceed at rates independent of acidity. Rate constants for the Cr(II) reductions of the pyridine and the several alkyl-substituted pyridine complexes, which must be reduced *via* outer-sphere paths, cluster in the range 10^{-3}–10^{-2} M^{-1} sec^{-1}. The corresponding Eu^{2+} reductions proceed an order of magnitude more rapidly, and the ratio of rates for the two reductants (0.04–0.12) applies not only to these pyridine derivatives, but also to N-bound complexes of isoquinoline and pyrazole and, in addition, to two of the three O-bound $(NH_3)_5Co^{III}$ complexes here

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(15) In an attempt to avoid complications associated with the use of $NOClO_4$, the reaction through the intermediate triethyl phosphate complex was prepared by heating the aquo complex with TEP in the presence of molecular sieves as described by R. J. Balahura and R. B. Jordan, *J. Amer. Chem. Soc.*, **92**, 1533 (1970). This method was erratic in our hands; in about half of the preparations, coversion to the TEP complex, or reaction with the heterocyclic ligand, was slow and incomplete.

(16) Reductions of the pyrazine complexes with small quantities of Cr^{2+} at acidities greater than 1.5 M yielded a white precipitate, as yet unidentified, which prevented spectrophotometric measurements of the reaction rate. Some turbidity was also encountered in the Eu(II) reductions, but this could be eliminated by prepeated recrystallization of the complex cobalt(III) perchlorates.

(17) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, Wiley, New York, N. Y., 1961, pp 49–50.

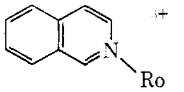
(18) This type of autocatalytic behavior has been reported for the Eu(II) reduction of the 4-carboxamidopyridine complex by C. Norris and F. R. Nordmeyer, *J. Amer. Chem. Soc.*, **93**, 4044 (1971).

Table III. Specific Rates for Chromium(II) and Europium(II) Reductions of Pentaamminecobalt(III) Complexes, $RCo(NH_3)_5^{3+}$[a]

R	$k_{Cr^{2+}}$	$k_{Eu^{2+}}$	$k_{Cr^{2+}}/k_{Eu^{2+}}$
	N-Coordinated Ligands		
Pyridine	0.0039[b]	0.083	0.047
3-Methylpyridine	0.0045[c]	0.038	0.12
4-Methylpyridine	0.0016[c]	0.039	0.041
3,5-Dimethylpyridine	0.0022[c]	0.036	0.061
3-Ethylpyridine	0.0046	0.067	0.069
4-Ethylpyridine	0.0026[c]	0.056	0.046
4-Phenylpyridine	0.0063	0.075	0.084
1,2-Bis(4-pyridyl)ethane	0.0086	0.15	0.057
1,2-Bis(4-pyridyl)ethylene (II)	<0.03[d]	<0.3[d]	
Imidazole (IV)	$<10^{-4}$ [e]	0.0063	
Pyrazole (V)	0.0023[f]	0.034	0.068
Isoquinoline (I)	0.0058	0.14	0.041
N,N-Dimethyl-3-carboxamidopyridine	0.029[f]	0.45	0.064
3-Carbomethoxypyridine	0.017	0.21	0.081
4-Carbethoxypyridine	1.3	<0.1[d]	>13
2-Methylpyrazine	150[g]	0.57	260
2,6-Dimethylpyrazine (III)	650	3.9	166
	O-Coordinated Ligands		
N,N-Dimethylformamide	0.0072[f]	0.067	0.11
2-Pyridone (VI)	0.12[h]	0.21	0.057
4-Pyridone	0.024[h]	0.086	0.28

[a] Specific rates in M^{-1} sec^{-1} at 25°, $\mu = 1.3$; values independent of acidity except for the complex of 2-methylpyrazine. [b] See ref 8b [c] See ref 13b. [d] Autocatalytic behavior observed (see text). [e] See ref 13a. [f] See ref 8a. [g] Limiting specific rate at low acidity. Observed rate constants are 120 in 1.4 M H^+ ($\mu = 1.5$), 139 in 0.45 M H^+, and 149 in 0.848 M H^+. [h] See ref 22. This and ref 8a present evidence that these ligands coordinate as pyridones (*e.g.*, VI) rather than as hydroxypyridines.

examined. This ratio, which, in the absence of an effective inner-sphere reduction path, is surprisingly insensitive to the nature of the organic ligand, may thus be considered to be characteristic of the metal centers. Since the standard potentials for the Cr^{2+}/Cr^{3+} and Eu^{2+}/Eu^{3+} couples are very nearly the same, the greater reactivity of Eu(II) may reasonably be attributed in part to the lower electrostatic barrier associated with reactions of the cation of greater radius with a positive oxidant. Moreover, the contraction of the bonds holding water molecules to the reducing metal center, which must precede the transfer of an electron from that center,[19] would be expected to be proportionately less for Eu^{2+} than for Cr^{2+}, and this factor would likewise favor reductions by the larger cation.



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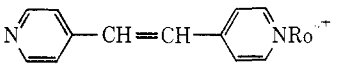

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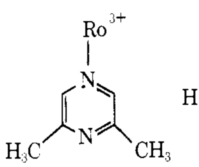

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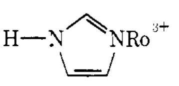

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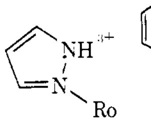

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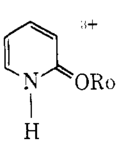

VI

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

Inner-Sphere Reductions. Three of the complexes in Table III react much more rapidly with Cr^{2+} than with Eu^{2+}, thus departing markedly from the reactivity pattern set by the others. Each of these three has a site which allows inner-sphere reduction and electron transfer through an extended conjugated system. The implication, then, is that when the structure of the oxidant allows reduction *via* an inner-sphere path, such a path is far more important for Cr^{2+} than for Eu^{2+}. Indeed, our experiments furnish no substantial evidence for participation of Eu^{2+} in inner-sphere reductions, although they do indicate that outer-sphere rates with this reductant, as with others,[20] are sensitive to the ligand environment about the oxidizing center.[21] Note that the ratio $k_{Cr^{2+}}/k_{Eu^{2+}}$ for the 3-$CON(CH_3)_2$-substituted pyridine derivative is 0.064, *i.e.*, well within the range characteristic of outer-sphere reduction by both reducing centers; this value confirms earlier evidence[22] that Cr(II) reduction of this complex is outer sphere. On the other hand, the Cr(II)/Eu(II) ratio for the 4-pyridone complex lies somewhat above this range, thus corroborating the evidence that this complex is reduced by Cr(II), in part, through a bridge mechanism. The outer-sphere contribution to the Cr(II) reduction of this complex has been estimated[22] to proceed at a specific rate of 0.0096 M^{-1} sec^{-1}, about $^1/_9$ the value here recorded for the Eu(II) reduction.

Chromium(II) reduction of the 4-carbethoxypyridine complex, in contrast to the rapidly reacting pyrazine derivatives, appears to yield $Cr(H_2O)_6^{3+}$ as the sole Cr(III) product (Table II). Thus although the enhanced reduction rate of this complex points to inner-sphere attack with formation of an ester-bound primary Cr(III) product, the known rapidity of aquation of such ester complexes under our conditions[23] prevents confirmation of this mechanism.

When the ester group is moved from the 4 to the 3 position, hence out of conjugation with the ring in-

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(19) See, for example, R. A. Marcus, *J. Chem. Phys.*, **24**, 970 (1956).

(20) See, for example, J. F. Endicott and H. Taube, *J. Amer. Chem. Soc.*, **86**, 1686 (1964).

(21) The predominance of the outer-sphere path for Eu^{2+} reductions is in accord with the notion that inner-sphere reduction requires a bond between the reducing cation and the lead-in atom with significant covalent character. On that basis, divalent rare-earth ions with their relatively large size and efficient nuclear screening, and with their f orbitals unavailable for effective hybridization, would be expected to react *via* the alternate path.

(22) E. S. Gould, *J. Amer. Chem. Soc.*, **90**, 1740 (1968).

(23) See, for example, J. K. Hurst and H. Taube, *ibid.*, **90**, 1174 (1968). A similar difficulty has been encountered in the study of reductions of acylpyridine derivatives.[8a]

trogen, even the kinetic evidence for inner-sphere reduction by Cr^{2+} disappears, for the Cr^{2+}/Eu^{2+} ratio observed for the 3-COOMe derivative lies close to the ratios for complexes of alkyl-substituted pyridines. The almost complete erosion of the inner-sphere path with change in substituent position is in accord with the situation observed with the more effectively mediating $-CONH_2$ group.[8b] When this substituent on $(NH_3)_5Co^{III}$-bound pyridine is relocated from the γ to the β position, inner-sphere reduction by Cr^{2+} is retarded by a factor of nearly 500. A similar attenuation of effect applied to the ester derivatives would lead to an inner-sphere path for the 3-COOMe complex having a rate constant of only $2.6 \times 10^{-3}\ M^{-1}\ sec^{-1}$, *i.e.*, about 15% of the observed specific rate.

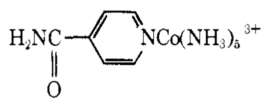
Substituted Pyrazine Complexes. In the substituted pyrazines here used as ligands, substituents lie α to one of the two ring nitrogens. Since these complexes are prepared under relatively mild conditions (Table I), coordination to Co(III) is assumed to occur at the less hindered 4-nitrogen (*e.g.*, III).

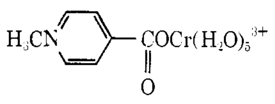
The slight acid dependency found for the Cr^{2+} reduction of the 2-methylpyrazine complex is almost certainly a medium effect, for it is not observed in the reduction of the more basic 2,6-dimethyl complex. Such a medium effect, resulting from changes in ionic environment as H^+ replaces Li^+ in the supporting electrolyte, is comparable in magnitude to those reported for other electron-transfer reactions in aqueous media.[24] Moreover, protonation of the uncoordinated nitrogen would not be expected to be kinetically significant in the range of acidities studied.[25]

The Cr(II) reductions of the methylated pyrazine complexes are found to be more rapid, by four to five powers of ten, than those of the various alkylated pyridine derivatives. Moreover, the Cr(III) products resulting from these reductions (Table II) are not $Cr(H_2O)_6{}^{3+}$, for they exhibit maxima at substantially higher energies than the hexaaquo ion. The spectral shifts are in the direction, and of the approximate magnitude, that would be expected to result from replacement of coordinated water with a ligand bonding through basic nitrogen. The observed rate enhancements, in conjunction with the nature of the Cr(III) products, thus provide very strong evidence that Cr(II) reduces the pyrazine complexes *via* a bridged mechanism with remote attack at the 4-nitrogen (which is in direct conjugation with the Co^{III}-bound nitrogen).

Since this lead-in site is hindered, the magnitudes of the specific rates are especially striking and confirm the unusual effectiveness of bound pyrazine in the role of redox mediator as observed earlier.[3b,13a,26]

Autocatalytic Reactions. Strong autocatalysis is observed here for three reactions, the reduction of the 4-carbethoxypyridine complex with Eu^{2+} and the reductions of the 1,2-bis(4-pyridyl)ethylene complex, II, with both Eu^{2+} and Cr^{2+}. Although we have not closely examined these reactions in the present study, we note the Eu^{2+} reductions to be very similar to the corresponding autocatalyzed reduction of the ring-bound amide derivative VII,[18] whereas the Cr^{2+} experiments with the ethylene complex II bring to mind the Cr(II) reductions of $(NH_3)_6Co^{3+}$, $(NH_3)_5pyCo^{3+}$, and $(NH_3)_5(DMF)Co^{3+}$ in the presence of the carboxylatochromium(III) complex VIII.[27] Kinetic treatments of both situations cited as analogous have been proposed, and evidence has been presented indicating the intervention of radical IX in the carboxamide reaction and radical cation X in the carboxylato-catalyzed reduction. Extension of earlier arguments[18] leads us to suggest that the active intermediate in the autocatalytic reduction of the ester complex, by Eu^{2+}, is radical XI (closely analogous to IX), formed by one-electron reduction of the free ligand, which, in turn, is released when the Co(III) oxidant is converted to the substitution-labile Co(II) complex.


VII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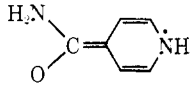
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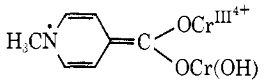
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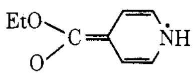
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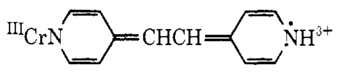
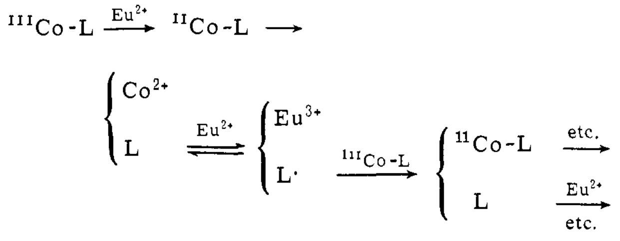

XII



L = 4-carbethoxypyridine

According to this interpretation, the observed autocatalysis reflects the increase in concentration of the

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(24) See, for example, (a) the reduction of $(NH_3)_5H_2OCo^{3+}$ with Cr(II) [D. L. Toppen and R. G. Linck, *Inorg. Chem.*, 10, 2635 (1971)]; and (b) the reduction of Pu^{VI} with Fe^{II} [T. W. Newton and F. B. Baker, *J. Phys. Chem.*, 67, 1425 (1963)].

(25) The 2,6-dimethyl complex, III, is derived from the more basic ($pK_a = 1.90$) of the pyrazine ligands. It is anticipated that coordination of $(NH_3)_5Co^{III}$ at one nitrogen would lower pK_a at the other site by about 4 units, *i.e.*, less drastically than coordination of H^+ (7 units decrease), but more markedly than coordination with $(NH_3)_5Ru^{III}$ (1.4 units decrease). Hence pK_a for the dimethyl complex is estimated at -2.0, with the value for the monomethyl complex still more negative. Supporting data are given by A. Albert in "Physical Methods in Heterocyclic Chemistry," Vol. I, A. R. Katritsky, Ed., Academic Press, New York, N. Y., 1963, pp 67–81; and by P. Ford, D. P. Rudd, R. Gaunder, and H. Taube, *J. Amer. Chem. Soc.*, 90, 1187 (1968). The latter contribution describes an instance in which coordination of a cation, $(NH_3)_5Ru^{II}$, at one nitrogen of pyrazine *increases* the basicity of the other but points out that this reversal of direction is neither expected nor observed with small tripositive centers.

(26) Preliminary studies by W. Movius and R. G. Linck (University of California, San Diego, 1970) indicate that the pyrazine complex of $(NH_3)_5Ru^{III}$ is reduced with Cr(II) over 4000 times as rapidly as the corresponding pyridine derivative.

(27) J. R. Barber, Jr., and E. S. Gould, *J. Amer. Chem. Soc.*, 93, 4045 (1971). Catalysis of this sort appears to be confined, thus far, to pyridine derivatives having a carbonyl or alkenyl substituent γ to the ring nitrogen.

free ligand (which is in rapid equilibrium with its reduced form, XI) as the reaction proceeds, and the dramatic acceleration of the reduction by addition of free ligand is in accord with this. The active species also rapidly reduces $(NH_3)_5pyCo^{3+}$, for which an inner-sphere path is structurally excluded, and an earlier study[27] indicates that such catalysts have only marginal effects in reductions where carboxyl is the only "lead-in" group present in the oxidant. We therefore suspect that the catalyzed reduction of the ester complex proceeds through an outer-sphere mechanism. In any event, the reducing species is remarkably reactive, for when present at much smaller concentrations than that of Eu^{2+}, it induces a reduction which may be 10^2 times as rapid as the uncatalyzed reaction.

A similar sequence can be invoked to account for autocatalysis in the Cr(II) reduction of the ethylene complex, with the proposed active intermediate the radical cation XII. The initial specific rate of reduction of this complex, when autocatalysis is minimal, lies below 0.03 M^{-1} sec^{-1}. The reduction must therefore be, in substantial part, outer sphere and should release the free ligand, which, again, in separate experiments, has been shown to accelerate the reduction. The one-electron Cr^{2+} reduction product from this ligand is represented as bound to Cr(III) in view of the ease with which Cr(II) is known to participate in inner-sphere reductions of conjugated organic species having donor centers.[12,13a,28]

The apparent absence of autocatalysis in the Cr(II) reduction of the 4-COOEt complex in this study, and the analogous 4-$CONH_2$ complex described by Nordmeyer,[8b] in contrast to the corresponding Eu(II) reductions, is in keeping with the suggestion that reduction of metal centers by radical or radical-ion intermediates of the type shown is principally an outer-sphere process if the only available mediating path features oxygen or nitrogen as a lead-in atom. Such mechanisms may become overshadowed if there is an alternate rapid inner-sphere path available to the reactants. On the other hand, such radicals may undergo inner-sphere oxidations in halide-containing systems, particularly in the absence of oxidizing metal centers. Thus, evidence has recently been presented[29] that radicals closely related to IX and XI reduce substituted benzyl halides *via* atom transfer.

In sum, although the present work leaves unanswered major questions related to the observed autocatalysis and to relationships between structure and reactivity in outer-sphere reactions, it serves to remind us that the mechanism of reaction involving a given oxidizing center may depend just as markedly on the identity of the reducing species as on the nature of mediating ligands. In reducing each of the several complexes having structures which offer an apparently attractive route for inner-sphere reduction, Cr(II), as expected, opts for bridging, whereas Eu(II) stubbornly clings to the outer-sphere path.

Acknowledgments. The authors are grateful to Professors Robert Linck, Henry Taube, and William Movius for permission to cite their data prior to publication and for valuable discussions.

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(28) Similarly, the reactive intermediates in the autocatalytic Eu^{2+} reductions (radicals IX and XI) are represented as species uncoordinated to metal ion centers in view of the evidence in the present study that reductions by Eu^{2+} greatly prefer the outer-sphere path. Moreover, even if the initial electron-transfer step were inner-sphere, the resulting Eu(III) product, a substitution-labile complex, would be expected to undergo immediate aquation.

(29) M. Mohammad and E. M. Kosower, *J. Amer. Chem. Soc.*, **93**, 2709 (1971).