Electron-Transfer Reactions of Cobalt(III). Relative Rate Comparisons and Free Energy Relations[1]

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Abstract: Data are presented for several $Ru(NH_3)_6^{2+}$ reductions of cobalt(III) complexes. The results reported demonstrate (1) that "nonbridging" ligand effects are of the same significance in outer-sphere as in inner-sphere reductions of cobalt(III), (2) that the reduction of $Co(NH_3)_5F^{2+}$ exhibits an acid dependence similar to that of $Co(NH_3)_5OH^{2+}$, and (3) that a unit change in charge of the cobalt complex does not alter the reactivity at high ionic strengths. The observations imply that the specific second-order rate constant, k_{12}, for electron-transfer reactions of cobalt(III) can be represented as the product of a contribution due to the cobalt complex and a contribution due to the reducing agent. It is shown that many of the different reactivity patterns for $Ru(NH_3)_6^{2+}$ (outer sphere) and Cr^{2+} (inner sphere) reductions of cobalt(III) complexes arise largely from the detailed differences in the free energies of reaction. It is postulated that the cobalt(III) center in the activated complex is very similar in outer-sphere and inner-sphere reactions, and this postulate provides a simple means of accounting for the acid-dependent reactivities of $Co(NH_3)_5OH^{2+}$ and $Co(NH_3)_5F^{2+}$.

For several years it has been the practice to distinguish between two limiting classes of activated complexes for electron-transfer reactions: (1) the outer-sphere activated complex in which no ligand (or ligands) is common to the coordination spheres of the reducing agent and the oxidizing agent, and (2) the inner-sphere activated complex in which one or more ligands are shared in the reactant coordination spheres[2] (for a recent review see ref 3). This mechanistic distinction has been clearly established only in some instances.[2-8] In many cases where the mechanisms have been established, *e.g.*, the $Ru(NH_3)_6^{2+}$[6] or $Cr(bipy)_3^{2+}$[4,5] (outer-sphere) reductions as opposed to the Cr^{2+}[2,3,7,9] (inner-sphere) reductions of cobalt(III) complexes, the outer-sphere and inner-sphere reducing agents exhibit vastly different patterns of reactivity as the ligands coordinated to the cobalt center are systematically changed.[2-5] Although there seems to be little agreement about the reasons for these different reactivity patterns, various relative rate comparisons have been suggested as being diagnostic of the reaction mechanism.[4-6,10] Some of these comparisons have received theoretical justification,[11] while others depend on experimentally established reactivity patterns, *e.g.*, toward $Co(NH_3)_5OH_2^{3+}$ and $Co(NH_3)_5OH^{2+}$[4,6] or $CO(NH_3)_5NCS^{2+}$ and $Co(NH_3)_5N_3^{2+}$.[10] In the case of the latter comparison, much of the difference in the reactivity of $Co(NH_3)_5SCN^{2+}$ and $Co(NH_3)_5N_3^{2+}$ toward inner-sphere reducing agents has been shown to be due to differences in the free energies of reaction.[12,13]

A more recent approach has been to examine the patterns of reactivity which result when the "bridging" ligand[14] is kept the same, but some "nonbridging" ligand[14] is varied in an oxidizing agent of the type $Co(en)_2AX^{2+}$ (where X is the "bridging" ligand and A is the single "nonbridging" ligand which is varied).[5,12-14] The cases so far reported involve the inner-sphere reduction of the cobalt(III) complexes with Fe^{2+}[15,16] or Cr^{2+}.[17] Previous investigators have variously stated that such "nonbridging" ligand effects should occur only in the case of inner-sphere reductions[15] (see also ref 7), and that similar "nonbridging" ligand effects should be observed in the case of outer-sphere reductions[16] of cobalt(III) complexes. In this paper we submit evidence which confirms the latter prediction: "nonbridging" ligand effects are very similar in inner-sphere and outer-sphere reductions of cobalt(III) complexes.

It would seem reasonable that reactivity patterns of cobalt(III) complexes should be related through a linear free energy relation as is so common in reactions of organic molecules.[18,19] One such free energy relationship has been proposed by Marcus[20] for the case of outer-sphere electron-transfer reactions. This relationship has been found to be reasonably applicable to these reactions[11,21-24] (with some exceptions,

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[2] H. Taube, *Can. J. Chem.*, 37, 129 (1959).

[3] A. G. Sykes, *Advan. Inorg. Chem. Radiochem.*, 10, 153 (1967).

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[5] J. P. Candlin, J. Halpern, and D. T. Trimm, *J. Am. Chem. Soc.*, 86, 1019 (1964).

[6] J. F. Endicott and H. Taube, *ibid.*, 86, 1686 (1964).

[7] N. Sutin, *Ann. Rev. Phys. Chem.*, 17, 119 (1966).

[8] J. P. Candlin, J. Halpern, and S. Nakamura, *J. Am. Chem. Soc.*, 85, 2517 (1963).

[9] H. Taube, H. Myers, and R. L. Rich, *ibid.*, 75, 4118 (1953).

[10] J. H. Espenson, *Inorg. Chem.*, 4, 121 (1965).

[11] (a) R. A. Marcus, *Ann. Rev. Phys. Chem.*, 15, 155 (1964); (b) *J. Phys. Chem.*, 72, 891 (1968).

[12] A. Haim and N. Sutin, *J. Am. Chem. Soc.*, 88, 434 (1966).

[13] A. Haim and N. Sutin, *ibid.*, 87, 4210 (1965).

[14] The nomenclature "bridging" and "nonbridging" will be used in this paper to refer to those ligands which are or are not, respectively, shared in the coordination spheres of the two metal centers *in the case of an inner-sphere* reaction. In cases of outer-sphere reactions, the ligands will also be referred to in this manner although they are not actually incorporated into the reactant coordination spheres.

[15] P. Benson and A. Haim, *J. Am. Chem. Soc.*, 87, 3826 (1965).

[16] C. Bifano and R. G. Linck, *ibid.*, 89, 3945 (1967).

[17] (a) R. D. Cannon and J. E. Earley, *ibid.*, 87, 5264 (1965); (b) *ibid.*, 88, 1872 (1966).

[18] J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1963.

[19] It should be noted that some success has been achieved in correlating the rates of some electron-transfer reactions with the stability constants of the complexes involved; see K. Bachmann and K. H. Lieser, Proceedings of the Symposium on Exchange Reactions, Brookhaven, IAEA, Vienna, 1965, p 29.

[20] For an outer-sphere reaction with specific rate k_{12}, $\log k_{12} \simeq {}^1/_2(\log k_1 + \log k_2 - \Delta G_{12}°/(2.303RT) + \log f_{12})$, where k_1 and k_2 are exchange specific rates, $\Delta G_{12}°$ is the standard free energy change of reaction, and $\log f_1 = (\log K_{12})^2/[4 \log (k_1k_2/Z_2)]$. See reference 11 and references contained therein.

especially in reactions involving cobalt(III) complexes[6,7,11,23]. In addition, this same relationship has found some application in correlating relative rates of reactions which proceed *via* an inner-sphere mechanism[7,11b,24] and can even be applied to organic and inorganic substitution reactions.[25,26] Although the Marcus relation has limitations and is not expected to give very precise correlations,[11,29] as noted above it has been reasonably successful in correlating rates of many electron-transfer reactions. In this paper we report a systematic attempt using the Marcus relation to examine the influence of changes in the free energy of reaction on the patterns of reactivity observed for inner-sphere and outer-sphere reductions of cobalt(III) complexes.[30] The approach adopted in this report, based on the similar "nonbridging" ligand effects observed in inner-sphere and outer-sphere reactions of cobalt(III) and using the Marcus relation to correlate rates, implies somewhat similar "activation" of the cobalt(III) center in both kinds of activated complex. This suggests a simple explanation of the similar acid dependence of the reactivities of $Co(NH_3)_5OH^{2+}$ and $Co(NH_3)_5F^{2+}$ in reactions of the outer-sphere type.

Experimental Section

Reagents. Solutions of $Ru(NH_3)_6^{2+}$ were prepared at the time of use by means of the Cr^{2+} reduction of $Ru(NH_3)_6Cl_3$.[6] The Cr^{2+} solution was prepared by the reaction of 3 *M* $HClO_4$ with a weighed amount of high-purity chromium metal.[33]

The following *cis*-cobalt(III) complexes were prepared as described in the literature: $[RH_2O]SO_4$,[15,34] $[RNH_3]Cl_2$,[15,34] $[RNH_2CH_2CH_3]Cl_2$,[35] $[RNH_2CH_2COOCH_3](ClO_4)_2$,[36] $[RNH_2CH_2COOH](ClO_4)_2$,[36] $[RNH_2CH_2C_6H_5]Cl_2$,[37] $[RNH_2C_6H_5]Cl_2$,[35] $[RNC_5H_5]Cl_2$,[35] $[RNH_2CH_2CH_2Br](ClO_4)_2$,[35b] and $[Co(NH_3)_5F](ClO_4)_2$;[38] $[RNC_5D_5]Cl_2$ was synthesized[35] using deuterated pyridine.

The infrared, visible, and ultraviolet spectra of these complexes were in good agreement with literature reports (to the extent that comparisons were possible).

Some of the cobalt(III) complexes employed in these studies are reported here for the first time, and details of their preparation and characterization are included below.

***cis*-Chlorocyclohexylaminebis(ethylenediamine)cobalt(III) Chloride, *cis*-$[Co(en)_2ClNH_2C_6H_{11}]Cl_2$.** *trans*-$[Co(en)_2Cl_2]Cl$ (2 g) was finely ground and suspended in 200 ml of DMF. Cyclohexylamine (1 ml) was added (30% excess) and the mixture warmed gently at 35–40° with slow stirring for 48 hr.[39] The solution turned a deep red color, and after cooling the red powder was filtered off and recrystallized by dissolving in a minimum of warm water and addition of a few drops of concentrated HCl. The mother liquor yielded more of the crystalline material when a small amount of ethyl alcohol was added.

The 60-Mc ^1H nmr spectrum in D_2O showed the presence of two different types of protons, in the ratio of 0.9:1. The ratio of ethylenediamine protons to cyclohexylamine protons in the complex is 0.73:1. Since one cyclohexylamine proton is closer to the cobalt(III) center, and is in this respect similar to the ethylenediamine protons, the ratio of downfield to upfield protons is expected to be 9:10, which is the actual value observed. The C_6H_{11} protons appear at δ 1.4 ppm (broad band) and ethylenediamine protons at δ 2.7 ppm with TMS as an external reference.

In the uv spectrum, a charge-transfer maximum could be observed at 2300 Å, as is generally the case for a chloropentamine-type complex.

***cis*-Chloro-β-aminopropionitrilebis(ethylenediamine)cobalt(III) Chloride, *cis*-$[Co(en)_2ClNH_2CH_2CH_2CN]Cl_2$.** The complex was prepared using the Bailar–Clapp method.[35] Recrystallization was achieved by dissolving the complex in a small amount of water and then adding ethyl alcohol and ether gradually. A dark red, microcrystalline material was obtained.

The infrared spectrum showed a C≡N stretch at 2240 cm^{-1}, which is also the value observed for the free ligand.

***cis*-Chloroethanolaminebis(ethylenediamine)cobalt(III) Chloride, *cis*-$[Co(en)_2ClNH_2CH_2CH_2OH]Cl_2$.** This complex was prepared by the Bailar–Clapp method.[35] Ultraviolet and visible spectral data for the above complexes are summarized in Table I.

Table I. Visible–Ultraviolet Spectra of Some *cis*-$[Co(en)_2ClA]^{2+}$ Complexes

A	Charge transfer λ_{max}, Å (ϵ)	Metal ion λ_{max}, Å (ϵ)
$NH_2C_6H_{11}$	2295 (1.99×10^4)	3675 (93.0), 5250 (83.4)
$NH_2CH_2CH_2OH$	2295 (2.24×10^4)	3675 (84.0), 5250 (76.4)
$NH_2CH_2CH_2CN$	2295 (2×10^4)	3675 (84.2), 5250 (77.4)

Kinetic Measurements. All solutions containing oxygen-sensitive reagents were kept under an atmosphere of scrubbed nitrogen.[6] In order to eliminate the catalytic effects of trace impurities,[6,40] special care was taken to purify the water for the reactions, and in most cases where solutions were transferred using a syringe technique the syringes were equipped with platinum needles. Cr^{2+} solutions were transferred using a Teflon needle attached to an all-glass syringe. Most of the details of the spectrophotometric and syringe techniques employed in the kinetic runs are described elsewhere.[6,41] The wavelength chosen to follow the decay of the absorbance of the cobalt(III) complex was generally about 500–550 mμ (for $k \leq \sim 5\ M^{-1}\ sec^{-1}$) or ~250 mμ (for $k > \sim 10\ M^{-1}\ sec^{-1}$) depending on the concentration of cobalt(III) oxidant,[6] which was always in excess. Under these conditions, reaction half-lives ranged from 5 min (for reduction of $Co(NH_3)_5F^{2+}$) to 40 sec (for reduction of *cis*-$Co(en)_2ClNH_2CH_2COOH^{2+}$ at $\mu = 1.0\ M$). Thus the time lapsed from the generation of $Ru(NH_3)_6^{2+}$ to the completion of a reaction was always less than 30 min. Under the conditions of our experiments, and in this length of time, solutions of $Ru(NH_3)_6^{2+}$ do not decompose to any significant extent.[40,42]

For reactions run at about 20° thermostating was accomplished using a thermostated cell holder with the Cary-14 spectrophotometer. For reactions run at other temperatures, in order to determine activation parameters, the reactions were run in a glass-jacketed thermostated cell. Reactant solutions were thermostated before mixing and the temperature of the product mixture was determined after reaction.

Specific rate constants for the second-order[40] reactions were calculated using data from over two reaction half-lives and a FORTRAN II least-squares program. In every case, excellent second-order kinetics were observed, the standard deviation in the rate constant resulting from the calculation being less than 2%.

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(21) W. L. Reynolds and R. W. Lumry, "Mechanisms of Electron Transfer," The Ronald Press Co., New York, N. Y., 1966.

(22) N. Sutin, *Ann. Rev. Nucl. Sci.*, 12, 285 (1962).

(23) G. Dulz and N. Sutin, *Inorg. Chem.*, **2**, 917 (1963).

(24) N. Sutin in Proceedings of the Symposium on Exchange Reactions, Brookhaven, ref 19, p 17.

(25) J. F. Endicott, unpublished observations.

(26) In addition, some very analogous correlations for organic substitution reactions have been known for some time.[18,27,28]

(27) C. G. Swain, *J. Am. Chem. Soc.*, 70, 1119 (1948); C. G. Swain and C. B. Scott, *ibid.*, **75**, 141 (1953); C. G. Swain, R. B. Mosely, and D. E. Brown, *ibid.*, 77, 3731 (1955); C. G. Swain, D. C. Dittmer, and L. E. Kaiser, *ibid.*, 77, 3737 (1955).

(28) J. O. Edwards, *ibid.*, **76**, 1540 (1954).

(29) R. A. Marcus, *J. Phys. Chem.*, **67**, 853 (1963).

(30) Some other systematic approaches to energy relationships involved in inner-sphere and outer-sphere activated complexes have been tried very recently. These include an attempt to classify changes in the stabilities of reactants and transition states in the two kinds of activated complex[31] and an attempt to develop a systematic approach to the energies involved in "nonbridging" ligand effects.[32] See also ref 19.

(31) A. Haim, private communication.

(32) R. G. Linck, private communication.

(33) H. Lux and G. Illman, *Chem. Ber.*, **81**, 2193 (1958).

(34) Where R = *cis*-$[Co(en)_2Cl]^{2+}$: A. Werner, *Ann.*, **386**, 165 (1912).

(35) (a) J. C. Bailar, Jr., and L. B. Clapp, *J. Am. Chem. Soc.*, **67**, 171 (1945); (b) S. C. Chan and F. Leh, *J. Chem. Soc.*, *A*, 760 (1966).

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(38) M. Linhard and M. Weigel, *Z. Anorg. Chem.*, **266**, 73 (1951).

(39) E. S. Gould, *J. Am. Chem. Soc.*, **89**, 5792 (1967).

(40) J. F. Endicott and H. Taube, *Inorg. Chem.*, **4**, 437 (1965).

(41) G. Svatos and H. Taube, *J. Am. Chem. Soc.*, **83**, 4172 (1961).

(42) H. Taube, private communication.

Results

A. "Nonbridging" Ligand Effects. The effect of variation of the ligand A on the specific rate of reduction of *cis*-$Co(en)_2ACl^{2+}$ with $Ru(NH_3)_6^{2+}$ is reported in Table II. Where possible the specific rates of $Ru(NH_3)_6^{2+}$ and Fe^{2+} reductions are compared.[43]

Table II. The $Ru(NH_3)_6^{2+}$ Reductions of *cis*-$Co(en)_2ClA^{2+}$ Complexes[a]

A	k,[b] M^{-1} sec^{-1}	pK_a of HX[c]	Log $k_{Ru(II)}$[d] $k_{Fe(II)}$
OH_2	231	0[e]	5.71
NH_3	12[f]	9.26	5.82
$NH_2CH_2CH_3$	32	10.8	
$NH_2CH_2CH_2OH$	34	9.5	
$NH_2CH_2CH_2CN$	63	7.7	
$NH_2CH_2CO_2CH_3$	73	7.6	
$NH_2CH_2CO_2H$	114[f]	9.7	
$NH_2CH_2CH_2Br$	175 ± 5	8.49	
$NH_2C_8H_{11}$	45.3 ± 0.3	10.66	
$NH_2CH_2C_6H_5$	37 ± 3	9.62	
$NH_2C_6H_5$	56 ± 8	4.6	
NC_5H_5	657 ± 7	5.17	5.91
NC_5D_5	683 ± 11		
OH_2[g]	$>10^5$		>5.6

[a] At 20 ± 0.5°, ionic strength (μ) = 0.1 M (NaCl), $[H^+] = 0.4\text{–}1.0 \times 10^{-3}$ M. [b] Specific rate constants determined for reactions first order in each reactant.[6] The values of k reported are those measured at an ionic strength of 0.1 M. For most of the oxidants listed here, specific rates were determined at several ionic strengths (catalytic effects seem most important at very low ionic strengths[40]), and these values extrapolated to 0.1 M are in very good agreement with the measured values. When two or more kinetic determinations have been performed at ionic strength of 0.1 M, the average value of k and the average deviation of the determinations are listed. The precision of the remaining rate constants (estimated from the deviations of least-squares slopes)[44] is ≤5%. [c] From D. D. Perrin, "Dissociation Constants of Organic Bases in Aqueous Solutions," Butterworth & Co., Ltd., 1965. [d] Data from ref 15 and 16 of this work. [e] Taking the activity of the solvent, H_2O, to be 1.[68] [f] The value of the specific rate constant interpolated from activation parameters of the reaction using six or more kinetic runs; see Table III. [g] For *trans*-$Co(en)_2ClOH_2^{2+}$. This reaction is still under investigation.

B. Acid-Dependent Reactivities of Cobalt(III) Complexes. The acid dependence of the specific rate constants for the $Ru(NH_3)_6^{2+}$ reductions of $Co(NH_3)_5F^{2+}$ and *cis*-$Co(en)_2Cl(NH_2CH_2CO_2)^+$ have been reported in Table III. In addition to the data reported in Table III, we have found the $Ru(NH_3)_6^{2+}$ reduction of $Co(NH_3)_5Br^{2+}$ acid independent over the same range of acidities as reported for the $Co(NH_3)_5F^{2+}$ reaction (μ = 0.2 M).

C. Activation Parameters. We have included in Table IV the activation parameters which we have determined for some of the reactions which are reported in this paper. The activation energy, E_a, and log A have been determined as the slope and intercept of the log of k *vs.* $1/T$ using a linear least-squares technique.[44] Error limits are least-squares estimates of the 95% confidence limits for the slope and intercept.

Table III. Acid Dependencies of the Reduction of Various Co(III) Complexes with $Ru(NH_3)_6^{2+}$ (22 ± 0.5°, μ = 0.2 M (NaCl))

$[H]^+$[a] $\times 10^3$ M	$[D^+]$[b] $\times 10^3$ M	k, M^{-1} sec^{-1} [c]	Complex
0.009[d]	...	0.27	$Co(NH_3)_5F^{2+}$
11.3	...	0.30	
43.3	...	0.37	
78.0	...	0.45	
155.0	...	0.53	
198.0	...	0.88	
...	0.009[d]	0.19	
...	62	0.43	
...	128	0.55	
...	205	0.97	
0.016–10	...	115 ± 6[e]	*cis*-$Co(en)_2Cl(H_2NCH_2CO_2)^+$
500[f]	...	474 ± 12[g]	
0.01[f]	...	390 ± 7[h]	

[a] [HCl] in H_2O. [b] [HCl] in D_2O. Concentrated HCl was added to 99.5% D_2O; the % H ≤5 in all cases. [c] Errors in the rate constant resulting from a least-squares treatment of the second-order plots are less than or about 3% of the tabulated values. [d] Sodium acetate–acetic acid buffer; Σ[acetate] = 0.045 M. [e] μ = 0.1 M (three determinations). [f] μ = 1.0 M. [g] Three determinations. [h] Two determinations.

D. ^{1}H Nmr Studies and Possible Induced Proton Exchange. Table II reveals the much greater reactivity of *cis*-$[Co(en)_2Cl\ pyridine]^{2+}$, as compared with the other amines listed in the table. The possibility of electron transfer *via* the aromatic ring seemed worth investigating. Localization of electronic charge on the ring could lead to exchange of the ring protons (deuterons) with the solvent deuterons (protons). In our experiments searching for evidence of electron-transfer-induced exchange of aromatic protons, we have examined aromatic ligands resulting from the $Ru(NH_3)_6^{2+}$ reduction of *cis*-$[Co(en)_2Cl(aniline)]^{2+}$ (which is not particularly fast) as well as from the reduction of *cis* $[Co(en)_2Cl(pyridine)]^{2+}$ which is fast.

$CrCl_2$ (0.60 mmole, 1.13 ml of 0.531 M $CrCl_2$ solution) was added to 0.662 mmole of $Ru(NH_3)_6Cl_3$ (204 mg dissolved in 7 ml of D_2O) to generate the corresponding $Ru(NH_3)_6Cl_2$ solution. This was added to 0.662 mmole (250 mg) of *cis*-$[Co(en)_2Cl(aniline)]Cl_2$ dissolved in 10 ml of 0.4 N DCl by means of a syringe. All operations were carried out under a scrupulously purified N_2 atmosphere. The reaction medium contained >90% D_2O. After 5 min, the resulting solution was made alkaline (pH 12) by the addition of concentrated NaOH, and extracted six times with 20-ml portions of CCl_4. The extract was dried over anhydrous Na_2SO_4 for 60 min and evaporated under vacuum until about 1 ml remained. The temperature was not allowed to exceed 35°. The final 30 ml of the distillation was carried out without heating. A theoretical yield of about 60 mg of aniline was expected. The actual amount recovered was much less.

The appearance of a C–D stretching frequency in the infrared could not be observed, and the nmr gave a strong signal showing the presence of aromatic protons. The ratio of *ortho*:*meta*:*para* hydrogens was found to be 2:2:1.

The same nmr results were obtained when a sample of aniline was dissolved in H_2O, the solution made alkaline with NaOH, extracted with CCl_4, and concentrated to 1 ml, and an nmr spectrum taken.

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(43) Some additional, preliminary observations[32] seem to extend the pattern deduced from Table II to some other cobalt(III) oxidants and possibly to yet another reducing agent.

(44) C. A. Bennett and N. L. Franklin, "Statistical Analysis in Chemistry and the Chemical Industry," John Wiley and Sons, Inc., New York, N. Y., 1954.

Table IV. Activation Parameters for Some $Ru(NH_3)_6^{2+}$–Co(III) Reactions (μ = 0.2 *M*)

Oxidant	pH	Temp range, °C[a]	E_a, kcal	Log *A*	ΔH, kcal	ΔS, eu
$Co(NH_3)_5F^{2+}$	5.04	10–30 (5)	14.0 ± 0.5	9.7 ± 0.3	13.4 ± 0.4	−16.8 ± 1.3
cis-$Co(en)_2Clgly^{2+}$	2.05	11–39 (7)	9.4 ± 0.8	9.1 ± 0.6	8.8 ± 0.8	−19.9 ± 2.8
cis-$Co(en)_2ClNH_3^{2+}$	2.7	13–35 (8)	12.1 ± 0.8	10 ± 0.6	11.5 ± 0.8	−15.4 ± 2.8

[a] Number of determinations in parentheses (approximately 5° intervals).

A similar experiment was carried out with *cis*-$[Co(en)_2ClC_5D_5N]Cl_2$, where the Co^{III} complex contained deuterated pyridine and the reaction was carried out in H_2O. A redox-induced exchange would be detected by the appearance of a C–H aromatic stretching and the C–C–H deformation frequencies in the ir, as well as the appearance of aromatic protons in the nmr (δ 6.3–7.2 ppm).

Since the boiling point of pyridine is much lower than that of aniline, the reaction solution was extracted with CS_2 and the procedure outlined above followed. The amount of pyridine recovered was determined by means of vpc and was found to be about 10 mg. The ir spectrum showed the absence of aromatic C–H stretch, and the nmr showed no aromatic protons. From a comparison of infrared frequencies in the region 1000–1300 cm^{-1}, it can be estimated that considerably less than 2% of the deuterium of NC_5D_5 had exchanged with H_2O.

Discussion

A. "Bridging" and "Nonbridging" Ligand Effects. In Table II we have compared the "nonbridging" ligand effects observed in the $Ru(NH_3)_6^{2+}$ reductions with the pK_a's of the ligands A and (where possible) with the specific rates of the Fe^{2+} reductions of the same cobalt(III) complexes. Although there may be a rough correlation between log *k* and pK_a, as suggested by Bifano and Linck,[16] it is apparent that this correlation is not appropriate to all the cases reported here. It should be mentioned, however, that the argument of Bifano and Linck[16] is applicable only if the value of 10*Dq* is either constant or increases as pK_a increases. In cases such as the alkylamine ligands, the value of 10*Dq* may be slightly lowered (possibly due to steric interactions)[25,45–47] relative to the 10*Dq* value for NH_3, and this may account for some of the minor variations of reactivity. It is also evident from Table II that the "size" of the ligand A is not the important factor in determining the reactivity of $Co(en)_2ACl^{2+}$; note especially that the reactivities are all about the same for A = aniline, ethylamine, or cyclohexylamine, while much greater reactivities are observed if A = pyridine or water.

It is evident from examination of the table that the specific rates of outer-sphere $Ru(NH_3)_6^{2+}$ and inner-sphere Fe^{2+} [16] reductions exhibit nearly the same sensitivity to the ligation of the cobalt(III) oxidant. It was most unexpected (at least to the present authors) that the relative reactivities of the $Co(en)_2ClA^{2+}$ oxidants are apparently unaffected by differences in the mechanism of reduction with $Ru(NH_3)_6^{2+}$ and Fe^{2+}. This similarity in the relative rates of reduction of $Co(en)_2ACl^{2+}$ complexes suggests that the specific rates of these electron-transfer reactions might be factorable into terms which involve the properties of the oxidizing agent and the reducing agent separately independent of mechanisms (*i.e.*, whether outer sphere or inner sphere); *i.e.*

$$k_{12} = fn_1(\text{cobalt}) \cdot fn_2(\text{reductant}) \qquad (1)$$

This is the approximate form of the free energy relationship suggested by Marcus[11,20,29] for outer-sphere reactions; as noted above, this relationship has found some application to inner-sphere reactions as well.

As we noted at the beginning of this paper, when the bridging ligands are varied the observed reactivity patterns for outer-sphere and inner-sphere reactions are vastly different. It now appears (from this study) that reactivity patterns may be nearly independent of mechanism when the bridging ligand is held constant. The obvious difference in the detailed mechanisms of inner-sphere and outer-sphere reactions (at least those involving cobalt(III)) is that the bridging ligand is ultimately transferred to the reducing agent in the former case and probably to the solvent in the latter case. If the immediate oxidized product of an inner-sphere reaction (say of *cis*-$Co(en)_2ACl^{2+}$ and Fe^{2+}) is a complex ion (such as $FeCl^{2+}$), then the free energy change associated with the electron-transfer step is different from the free energy change which results if the uncomplexed metal ion (*e.g.*, Fe^{3+}) is the product. This difference can be accounted for by adding to the free energy change of the latter reaction (*i.e.*, with Fe^{3+} as a product) a term proportional to the formation constant of the complex ion[49] resulting from the former reaction ($FeCl^{2+}$, in the example). When the above argument is represented in terms of standard oxidation potentials, as is done below, it is of utmost importance to choose the standard state for the formation constants consistent with established oxidation-state conventions.[49,50] In the following discussion we have employed the Marcus relation[20] in order to systematically analyze the effect of differences in the free energy of reaction on the different reactivity patterns which are observed for outer-sphere and inner-sphere reactions. In our view this approach is an exploratory effort in the systematization of reactivity patterns in electron-transfer reactions.

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(45) M. Paris and N. F. Feiner, *Inorg. Nucl. Chem. Letters*, 3, 337 (1967).

(46) S. C. Chan and K. Y. Hui, *Australian J. Chem.*, 20, 2529 (1967).

(47) It should also be noted that variations in pK_a only approximate the variations in proton affinity which Bifano and Linck would probably have preferred to use.[16] A means for calculating a quantity more appropriate than pK_a has recently been suggested by Klopman.[48]

(48) G. Klopman, *J. Am. Chem. Soc.*, 90, 223 (1968).

(49) W. Latimer, "Oxidation Potentials," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1952.

(50) As observed by a referee. The conventions employed here are those of Latimer,[49] the most important being unit activity in the predominant species, zero ionic strength, and *T* = 25°. It is important to observe that the relevant values of K_f are very scarce in the literature, and in some of our calculations we have been forced to use values of K_f obtained at high ionic strengths or $T \neq 25°$. Since in this paper we wish to explore the grosser features of an unusual correlation, we have not complicated the argument by attempting to estimate discrepancies arising from variations in ionic strength or temperature. In some cases these discrepancies can amount to a factor of the order of 10 in calculated values of k_{12}.

Table V. Reactivities of $Co(NH_3)_5X^{2+}$ and $Co(NH_3)_5XH^{3+}$ toward Various Reducing Agents. Calculated and Observed Patterns

Oxidant complex	$^1/_2$[log f_1(cobalt)][a]	Reductant	$^1/_2$ log k_2[b]	8.45 log $E_2°$ [c]	Log k_{12} (calcd)[o]	Log k_{12} (obsd)
$Co(NH_3)_5OH_2^{3+}$	−0.13	Cr^{2+}	−3.25[d]	3.46	0.08	−0.3[e]
		V^{2+}	−1.48[d]	2.16	0.55	−0.3[e]
$Co(NH_3)_5OH^{2+}$	−2.05	Cr^{2+}	−0.076[f]	8.51[g]	6.38	6.18[e]
		V^{2+}	0.13[h]	7.7[g]	5.52[i]	≤5.87[j]
		V^{2+}	−1.48[d,k]	2.16[k]	−1.37[k]	≤5.87[j]
$Co(NH_3)_5FH^{3+}$	0.78[l]	Cr^{2+}	−3.25[d,k]	3.46[k]	1.04	...
		V^{2+}	−1.48[d,k]	2.16	1.46	...
		Fe^{2+}	0.3[k]	−6.5[k]	−5.42	...
$Co(NH_3)_5F^{2+}$	−1.22	Cr^{2+}	−0.83[e]	6.09[m]	4.04	5.4[n]
		V^{2+}	−1.48[d,m]	2.16[m]	−0.54[k]	0.41[e]
		Fe^{2+}	0.80	−3.46	−3.88	−2.18[e]

[a] $^1/_2 \log[f_1(Co)] = \log k_{12} - {}^1/_2 \log k_2 - 8.45E_2°$ for the $Ru(NH_3)_6^{2+}$ reduction of the various oxidants. Values of k_{12} are either from this work or ref 6. The value of k_2 at 0.1 M ionic strength has been taken to be 10^3 M^{-1} sec^{-1}.[52] The value of $E°$ for the $Ru(NH_3)_6^{2+,3+}$ couple has been taken to be −0.10 V.[52] [b] Values taken from F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1967, and references cited therein. [c] Reference 49. [d] Estimated from the Marcus relationship[20] using data for the reduction of $Ru(NH_3)_6^{3+}$ at $\mu = 0.2$ M,[6] using parameters listed in footnote *a* above. The exchange rate constants calculated in this manner are lower than or equal to the upper limits found in the literature ($k_{V^{2+,3+}} \simeq 10^{-2}$ sec^{-1} [K. V. Krishnamurty and A. C. Wahl, *J. Am. Chem. Soc.*, **80**, 5921 (1958)], and $k_{Cr^{2+,3+}} \leq 2 \times 10^{-5}$ M^{-1} [A. Anderson and N. A. Bonner, *ibid.*, **76**, 3826 (1954)], which is to be expected as the latter were determined at very high ionic strengths. [e] $\mu = 1.0$ M, 25°. [f] $\mu = 1.0$ M, 24.5°. [g] Calculated from the standard potential of the M^{2+}/MOH^{2+} couple using the values of pK_a = 3.95 (μ = 0, 25°)[56] and pK_a = 2.7 (μ = ?, 25°)[56] for Cr^{3+} and V^{3+}, respectively. [h] $\mu = 2$ M, 25°. [i] Value estimated assuming inner-sphere mechanism. [j] A. M. Zwickel and H. Taube, *J. Am. Chem. Soc.*, **83**, 793 (1961). [k] Value estimated assuming an outer-sphere mechanism. [l] Calculated assuming that the ratio of reactivities for $Co(NH_3)_5F^{2+}$ and $Co(NH_3)_5FH^{3+}$ is about the same as the ratio of reactivities of $Co(NH_3)_5OH^{2+}$ and $Co(NH_3)_5OH_2^{3+}$ toward $Ru(NH_3)_6^{2+}$. This implies that the pK_a of $Co(NH_3)_5FH^{3+}$ is ∼−1. The slightly higher acidity implied for $Co(NH_3)_5FD^{3+}$ than for $Co(NH_3)_5FH^{3+}$ is consistent with a very low pK_a (R. P. Bell, "The Proton in Chemistry," Cornell University Press, Ithaca, N. Y., 1959). [m] Calculated from the standard potential of the M^{2+}/MF^{2+} couple using values of log K = 5.20 (μ = 0, 25°) and log K = 6.05 (μ = 0, 25°) for the stability constant of CrF^{2+} and FeF^{2+}, respectively.[56] [n] $\mu = 0.1$ M, 25°. [o] Log k_{12} [(log f_1)/2] + $^1/_2$ log k_2 + 8.45$E_2°$.

If, in combining the Marcus relation with (1) we ignore to a first approximation the f_{12} terms, then (at 25°)

$$\log (fn_1) \cong 2 \log (k_{12}) - \log (k_2) - 16.9\ E_2° \quad (2)$$

For $Ru(NH_3)_6^{2+}$, evaluation of the fn_2 term is simple in the sense that neither k_2[51] nor $E_2°$[51] depend on Cl^-. In the case of the Fe^{2+} reactions it is necessary to use the specific rate of the $FeCl^{2+}/Fe^{2+}$ exchange reaction for k_2' and the standard potential for the $FeCl^{2+}/Fe^{2+}$ couple for $E_2°'$. Literature data permit us to estimate $k_2' = 22.8$ M^{-1} sec^{-1} [53,54] and (using log K_f = 1.35 for $FeCl^{2+}$)[56] $E_2°' = -0.69$ V. If one uses the specific rate of the $Ru(NH_3)_6^{2+}/Co(NH_3)_5Cl^{2+}$ reaction[6] and the appropriate values of k_2 and $E_2°$ [51] to find a value for log $(fn_1)/2$, then this with the values of k_2' and $E_2°'$ appropriate to the $FeCl^{2+}/Fe^{2+}$ couple permits one to estimate that the specific rate of the $Fe^{2+}/Co(NH_3)_5Cl^{2+}$ reduction should be approximately 4×10^{-4} M^{-1} sec^{-1}. The measured value, $k_{12} = 1.35 \times 10^{-3}$ M^{-1} sec^{-1},[57] is reasonably close to this estimate; although the ionic strength dependence of the $Fe^{2+}/Co(NH_3)_5Cl^{2+}$ reaction is expected to be relatively weak,[6,23] k_{12} at 0.2 M ionic strength is undoubtedly slightly less than 10^{-3} M^{-1} sec^{-1}.[58] It certainly seems that most of the difference in reactivity toward $Co(NH_3)_5Cl^{2+}$ between $Ru(NH_3)_6^{2+}$ and Fe^{2+} lies in the differing free energy changes involved. In order to examine the hypothesis that a free energy correlation does exist for electron-transfer reactions, we have used data from the literature to compare observed specific rates of reduction of cobalt(III) complexes for a variety of reducing agents to the specific rates calculated (as above) assuming a free energy correlation (2) for these electron-transfer reactions (Tables V and VI).

It can be seen from Table V that the acid-dependent reactivities of $Co(NH_3)_5OH^{2+}$ in outer-sphere (*i.e.*, $Ru(NH_3)_6^{2+}$) and inner-sphere reactions are indeed correlated through simple free energy relations (eq 1 and 2). The correlation of the reactivities of Cr^{2+} and $Ru(NH_3)_6^{2+}$, in which case the reaction mechanism is well established,[6,59] toward $Co(NH_3)_5OH_2^{3+}$, $Co(NH_3)_5OH^{2+}$, and $Co(NH_3)_5F^{2+}$ is certainly far better than expected. It can be seen from Table V that it is the very great stability of $CrOH^{2+}$ (the presumed immediate Cr(III) product of the electron-transfer reaction) which

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(51) Values chosen for k_2 and $E_2°$ in this case are ∼10^3 M^{-1} sec^{-1} and −0.1 V on the Latimer scale.[49,52]

(52) T. Myer, quoted in L. E. Bennett and H. Taube, *Inorg. Chem.*, 7, 254 (1968).

(53) N. Sutin, J. K. Rowley, and R. W. Dodson, *J. Phys. Chem.*, **65**, 1248 (1961).

(54) The FeX^{2+}/Fe^{2+} exchange reactions pose a small problem of consistency since it has been shown that the $FeCl^{2+}/Fe^{2+}$ reaction proceeds only about 70% through an inner-sphere path.[55] The FeF^{2+}/Fe^{2+} reaction presumably proceeds mostly through an inner-sphere path.[7] A reasonable extrapolation would be that the $FeBr^{2+}/Fe^{2+}$ reaction proceeds mostly through an outer-sphere path. Since distribution of activated complex geometries for $Co(NH_3)_5X^{2+}/Fe^{2+}$ reactions is not unambiguously established, we have not attempted to estimate k_2 for FeX^{2+}/Fe^{2+} reactions of only inner-sphere activated complexes. To indicate the effect of such variations of mechanism we have estimated log k_{12} for both outer-sphere and "inner-sphere" (our estimate is certainly a maximum value) Fe^{2+} reductions of $Co(NH_3)_5Br^{2+}$ in Table VI. This ambiguity of mechanism does not exist for the analogous Cr^{2+} reductions, and investigations of the Cr^{2+} reductions of oxidants listed in Table II are in progress.

(55) R. J. Campion, T. J. Conocchioli, and N. Sutin, *J. Am. Chem. Soc.*, **86**, 4591 (1964).

(56) L. G. Sillen, "Stability Constants for Metal-Ion Complexes," Special Publication No. 17, The Chemical Society, London, 1964.

(57) (a) J. H. Espenson, *Inorg. Chem.*, **4**, 121 (1965); (b) H. Diebler and H. Taube, *ibid.*, **4**, 1029 (1965).

(58) Since the measurements of k_{12} were made at $\mu = 1.0$ ionic strength while the rates of the $Ru(NH_3)_6^{2+}/Co(NH_3)_5Cl^{2+}$ [6] and the exchange reactions[37,40] all were determined at lower ionic strengths. A somewhat less important discrepancy can arise because values of K_{12} are generally referred to zero ionic strength.[55] This error is minimized in our handling of II since the factor correcting K_{12} from 0 to 0.1 M ionic strength is partly contained in the unevaluated fn_1 terms. There is no question that a completely rigorous test of the correlation II would refer all measured quantities to identical standard conditions (preferably 25°, zero ionic strength, etc.).[50] Such data are not available.

(59) W. Kruse and H. Taube, *J. Am. Chem. Soc.*, **82**, 526 (1960).

Table VI. Comparison of Calculated and Observed[a] Rates for $Co^{III}(NH_3)_5X + M^{n+} \longrightarrow MX^{m+} + Co^{II} + \ldots$ (i)[b] and $Co^{III}(NH_3)_5X + M^{m+} \longrightarrow M^{(m+1)+} + Co^{II} + X + \ldots$ (o)

		Reducing agent				
X	$^1/_2$ log $[f_1(Co)]$[c]	Fe^{2+} Log k_{12}[d]	Cr^{2+} Log k_{12}[e]	Cu^+ Log k_{12}[f]	V^{2+} Log k_{12}[g]	Eu^{2+} Log k_{12}[g]
I^-	3.17		~4[h] (i)	>3 (i)	3.8 (o)	
			(6.5)	~1.5 (o)	(2.08)	
		<−2.3 (i)	~4.7 (i)	>2 (i)	3.22 (o)	
Br^-	2.54	−3.7 (o)	(6.2)	0.9 (o)		
		(−3.25)		(6 ± 1)	(1.40)	
Cl^-	1.76	−3.38 (i)	6.04 (i)		2.4 (o)	~3.5 (i)
		(−2.87)	(5.8)		(~0.7)	(2.6)
F^-	−1.22	−3.88 (i)	4.04 (i)		−0.54 (o)	
		(−2.18)	(5.4)		(0.41)	
		−1.73	4.5 (i)	>0.3 (i)	0.60 (i)	
N_3^-	−0.58[j]			−2.2 (o)	~2.6 (o)	
		(−2.06)	(~5.5)	(3.6)[i]	(1.11)	
			6.38 (i)		5.5 (i)	
OH^-	−2.05	−1.1 (i)			−1.37 (o)	
			(6.18)		(≤5.87)	
OH_2	−0.13	−6.3	0.08		0.55	~1.0
			(−0.3)	~−1	(−0.3)	(−0.8)
NH_3	−2.65	−8.9	−2.44		−0.03	~−1.5
			(−4.1)	~−4	(−3.7)	(−1.7)

[a] Log of observed specific rates in parentheses. Abbreviations: i = inner; o = outer. [b] Stability constants of MX^{m+} are from ref 56 and references cited therein except as noted. [c] Calculated from (2) using k_{12} as reported in this study or ref 6; see footnote *a*, Table V. [d] Observed values of k_{12} from ref 7, 15, 16, 21, and 57 and references cited therein. $Fe^{2+}/Fe^{III}X$ exchange specific rates are from ref 21 and references cited therein. [e] Observed values of k_{12} and $Cr^{2+}/Cr^{III}X$ exchange specific rates are from F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1966, and references cited therein. [f] Observed values of k_{12} are estimates from ref 6 and 25. The Cu^+/Cu^{2+} exchange specific rate is estimated as ~0.3 M^{-1} sec^{-1} using the parameters listed in footnote *a*, Table V, and free energy correlation 2. [g] Observed values of k_{12} are from ref 5 and 7 and references cited therein. The values of ~1 × 10^{-3}, 2.6 × 10^{-4}, and 10^{-5} M^{-1} sec^{-1} have been used for the V^{2+}/V^{3+}, $Eu^{2+}/EuCl^{2+}$, and the Eu^{2+}/Eu^{3+} exchange specific rates, respectively: D. J. Meier and C. S. Garner, *J. Phys. Chem.*, **56**, 853 (1952); A. Adin and A. G. Sykes, *J. Chem. Soc.*, 1230 (1966). [h] This is a guess based on trends of stability constants and exchange specific rates for the halo complexes of Cr(III). [i] J. F. Endicott and H. Taube, unpublished observations. Estimated from the initial rate of the $Cu^+/Co(NH_3)_5N_3^{2+}$ reaction with an excess of $Co(NH_3)_5N_3^{2+}$. This reaction is not exactly stoichiometric as Cu^+ reacts faster with N_3^- than with $Co(NH_3)_5N_3^{2+}$. [j] Since the kinetics of the $Ru(NH_3)_6^{2+}/Co(NH_3)_5N_3^{2+}$ reaction are complicated by the rapid $Ru(NH_3)_6^{2+}/N_3^-$ reaction,[6] it is not known whether the former is acid dependent.

accounts for most of the difference in reactivity of $Co(NH_3)_5OH_2^{3+}$ and $Co(NH_5)_5OH^{2+}$ toward Cr^{2+}. A similar acid-dependent reactivity of $Co(NH_3)_5OH^{2+}$ should be observed for Fe^{2+} (see Table V) and is probably not observed in the case of V^{2+} (Table V) because substitution into the coordination sphere of V^{2+} is too slow.[60-62]

The third entry, for the hypothetical $Co(NH_3)_5FH^{3+}$, is included in Table V to use II to predict that in the case of inner-sphere reductions of $Co(NH_3)_5F^{2+}$ no acid dependence should be observed as $Co(NH_3)_5F^{2+}$ is the predominant species in solution,[63] protonation of this complex should interefere with formation of a F^- bridged intermediate, and some of the gain in free energy due to transfer of F^- from cobalt to the Fe(III) or Cr(III) (for example) product would be lost.

One additional point is illustrated by the data in Table V: since for the case of $Co(NH_3)_5OH_2^{3+}$ there is no means of clearly distinguishing inner-sphere from outer-sphere reactions in terms of the simple free energy correlation (note that in the cases of V^{2+} and Cr^{2+} both exchange reactions are outer sphere), eq 2, the discrepancy between observed and calculated values of k_{12} in this case may indicate a 1-2 kcal/mole difference in activation free energy for inner-sphere and outer-sphere activated complexes.

It can be seen from data tabulated in Tables II, V, and VI that the factorization (1) and the free energy correlation (2) of inner-sphere and outer-sphere reaction rates are satisfactory over a range of about 10^9 in reactivity and for a large variety of cobalt(III) oxidants. In some cases data for stability constants and exchange rates are either totally lacking, or different reports disagree too much to permit us to use (2) in estimating k_{12}. Data for Cu^+ reactions are included to illustrate the order of reactivities which is expected for inner-sphere *vs.* outer-sphere mechanisms (assuming that log $K_{stab} > 1$ for CuX^+ and/or that the exchange rate of CuX^+/Cu^+ is much greater than that of Cu^{2+}/Cu^+). It is most unexpected that *all* the outer-sphere rates calculated for the V^{2+} reductions of cobalt(III) complexes are significantly (generally ~ 10^2) greater than the rates actually observed.[64]

B. Effect of Variation of Charge on Reactivity. The variation of the specific rates of reaction with the ionic strength of the solution is well known.[40,65,66] The variation of reactivity of a complex due to the change in its charge type at high ionic strengths is much more difficult to establish experimentally. Since we have been examining a free energy correlation in ionic reactions where the charge of the cobalt(III) oxidant is sometimes +3 and sometimes +2, it is important to assess the significance of this variation of charge on the observed

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(60) J. M. Malin and J. H. Swinehart, *Inorg. Chem.*, 7, 250 (1968).

(61) H. J. Price and H. Taube, *ibid.*, 7, 1 (1968).

(62) W. Kruse and D. Thusius, *ibid.*, 7, 464 (1968).

(63) Our attempts to determine a pK_a for $Co(NH_3)_5FH^{3+}$ failed because of the acid-catalyzed hydrolysis of $Co(NH_3)_5F^{2+}$.

(64) If an outer-sphere rate is faster than an inner-sphere rate, then the outer-sphere rate is observed (see discussion in ref 3 and 8). That a similar phenomenon is not observed for Cr^{2+} reactions may be due to the rapid substitution on Cr^{2+} [7] (as opposed to V^{2+} [59-62]).

(65) R. Fowler and E. A. Guggenheim, "Statistical Thermodynamics," Cambridge University Press, London, 1956.

(66) A. R. Olson and T. R. Simonson, *J. Chem. Phys.*, 17, 1167 (1949).

rate of reaction. Our approach to this problem has been to investigate the acid dependence of the reactivity of *cis*-$Co(en)_2Cl(NH_2CH_2CO_2)^+$. The p$K_a$ (of the carboxylate function) of the coordinated glycine ($-NH_2CH_2CO_2H$) has been determined to be 2.1 and can be compared to a pK_a of 2.3 for the free ligand.[36] Thus in this case the standard free energy change involved in the reductions of $Co(en)_2Cl(NH_2CH_2CO_2)^+$ and $Co(en)_2Cl(NH_2CH_2CO_2H)^{2+}$ should be about the same (as opposed to the case of $Co(NH_3)_5F^{2+}$; see below) and variations in reactivity may be reasonably ascribed to a change in charge of the complex. Since the reaction with $Ru(NH_3)_6{}^{2+}$ exhibits little acid dependence,[67] it may be concluded that a solution 0.1 *M* in ionic strength effectively shields (electrostatically) the reactants from one another.

C. Some Implications and Interpretations of the Correlations 1 and 2. An important assumption in the factorization 1 is that the cobalt(III) center is very similar (±1 or 2 kcal; see A above) in the activated complexes for inner-sphere and outer-sphere reactions.[69] If one considers the limit that the cobalt center is the same in both activated complexes, then the two classes of reactions could be formally written

$$Co(NH_3)_5X^{2+} + M^{2+} \longrightarrow Co(NH_3)_5{}^{2+} + X^-(aq) + M^{3+} \quad \text{(outer sphere)}$$

$$Co(NH_3)_5X^{2+} + M^{2+} \longrightarrow Co(NH_3)_5{}^{2+} + MX^{2+} \quad \text{(inner sphere)}$$

Although it is not necessary that the two immediate cobalt(II) products be identical, it is useful to consider this limiting case since this gives some insight into the acid-dependent reactivities of $Co(NH_3)_5OH^{2+}$ and $Co(NH_3)_5F^{2+}$. In these cases, if we assume that the immediate products of outer-sphere reduction of the cobalt(III) complexes include H_2O and HF, respectively, then the free energy of activation of the cobalt center in these cases would involve a contribution due to the free energy of protonating OH^- or F^-.[72] This energy contribution is easily large enough to account for the differences in reactivity of the protonated and unprotonated complexes even if the Co^{III}–X bond is not completely broken in the activated complex.

Since the Marcus cross relation (especially neglecting $f_{12}{}^{20}$) is only approximate in the first place,[11,29] since several additional terms may be neglected in applications of the Marcus relation to inner-sphere reactions,[11b,74] and since the free energy relation 2 proposed above neglects a contribution due to a (probably fractional) contribution of the solvation free energy of the bridging ligand X,[75] we regard a difference of unity between log k_{12}(observed) and log k_{12}(correlated) as excellent agreement. It is our hope that continued systematic studies and careful logical analyses will eventually lead to a precise free energy correlation of electron-transfer reactions.

For the present, the reasonable correlation (as far as can be judged)[50,54,58] with Fe^{2+}, Cr^{2+}, Cu^+, and Eu^{2+} reactions (Tables II and VI) indicates that the approach is successful to at least an order of magnitude in k_{12}. Thus there can be little doubt that one of the most common and important ways in which a bridging ligand can affect the rate of an electron-transfer reaction is by significantly changing the free energy of reaction. It must be regarded as a major success of this correlation that it leads to a simple and entirely reasonable explanation of the acid-dependent reactivity of $Co(NH_3)_5OH^{2+}$ toward both Cr^{2+} and $Ru(NH_3)_6{}^{2+}$. This clearly shows that it is not necessary to assume that a ligand such as OH^- exhibits extraordinary conductivity behavior in electron-transfer reactions.

The failure of the correlation II to predict *outer-sphere* rates for Cr^{2+} and V^{2+} reductions of cobalt(III) complexes is a surprise. We are inclined to regard this as a manifestation of selection rules which may be operative in electron-transfer reactions. This suggestion will be explored in a different publication.[76]

Conclusions

It has been shown that for electron-transfer reactions of cobalt(III) complexes (1) the specific rate constant can be approximately factored into contributions of the cobalt(III) oxidant and of the reductant-independent of mechanisms

$$k_{12} \simeq fn_1(\text{cobalt}) \cdot fn_2(\text{reductant})$$

and (2) the specific rate constants are correlated through a linear free energy relation—approximately through the Marcus relation—nearly independent of mechanism.

These observations have been interpreted as indicating (1) that the cobalt(III) center is very similar in the activated complexes for both outer-sphere and inner-sphere reactions, (2) that the detailed accounting of free energy changes is different for outer-sphere and inner-sphere reactions, and (3) that the specific function of a bridging ligand in facilitating electron transfer is largely

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[67] The ~20% higher rate for this reaction when $[H^+] = 0.5$ *M* than when $[H^+] \sim 10^{-4}$ *M* ($\mu = 1.0$ *M*, see Table III) may be due to (1) changes in the activities of reactant species when the composition of the ionic medium is altered so greatly,[68] (2) a medium dependence of the free energy of activation, or (3) a slightly greater reactivity of the protonated complex. This matter is still under investigation.

[68] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolyte Solutions," Reinhold Publishing Corp., New York, N. Y., 1958.

[69] The similarity is, of course, in the contribution of the cobalt(III) center to the free energy of activation. Diebler, *et al.*,[70] have shown that the $Co^{III}-OH_2$ bond is stretched to different extents in the outer-sphere and inner-sphere reductions of $Co(NH_3)_5OH_2{}^{3+}$. It seems important to note, however, that (1) there is bond stretching for both geometries of the activated complex and (2) that the $Co^{III}-OH_2$ and $Co^{III}-NH_3$ stretching frequencies[71] are not greatly different (*i.e.*, there may be some Co–N bond stretching in the outer-sphere activated complex for reduction of $Co(NH_3)_5OH_2{}^{3+}$). Studies currently in progress are expected to clarify these points.

[70] H. Diebler, P. H. Dodel, and H. Taube, *Inorg. Chem.*, **5**, 1688 (1966).

[71] K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963.

[72] An alternative interpretation is that the activated complex is nearly the same for all $Co^{III}(NH_3)_5X$ complexes (regardless of X), and greater stability of $Co(NH_3)_5OH^{2+}$ (compared to $Co(NH_3)_5OH_2{}^{3+}$) and $Co(NH_3)_5F^{2+}$ (compared to $Co(NH_3)_5FH^{3+}$) is responsible for the acid-dependent reactivity of these complexes. It is also to be noted that the most reasonable guess (*e.g.*, using the correlation suggested by Rock[73]) as to the variation of oxidation potential of the Co(II)–Co(III) couples is that the protonated complexes are weaker oxidants than their conjugate bases.

[73] P. A. Rock, *Inorg. Chem.*, 7, 837 (1968).

[74] However, we see no reason to *assume* strong electronic coupling between metal centers only because the activated complex for an electron-transfer reaction has an inner-sphere geometry.

[75] This contribution arises if a model is assumed in which the ligand X is partly removed from the cobalt(III) center to the solvent in the activated complex for outer-sphere electron-transfer reactions; see preceding discussion. Aspects of this model will be treated with greater rigor elsewhere.

[76] J. F. Endicott, in preparation.

due to an increase in the free energy of reaction by forming a relatively unstable cobalt(III) complex and/or a relatively stable MX^{n+} product. Other functions of bridging ligands (*e.g.*, changing the path of reaction, altering selection rules, varying the lifetimes of bridged intermediates, etc.) are much less obvious and will be considered elsewhere.

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Proton Magnetic Resonance Studies of Amino Acid Complexes of Platinum(II). I. Synthesis, Spectral Interpretation, and Conformational Implications[1]

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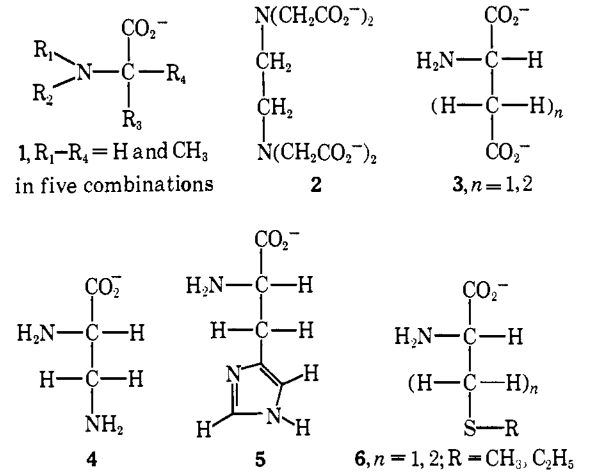
Abstract: Proton nmr spectra of Pt(II) complexes of six different types of amino acids (**1–6**) have been analyzed. The effects of coordination and of proton titration on chemical shifts of skeletal protons and the presence or absence of ^{195}Pt side bands have been used to determine the coordination sites in multidentate ligands. Several different types of isomerism, including that resulting from creation of a new asymmetric center by coordination to the metal atom, are revealed by the spectra. A strong conformation dependence for ^{195}Pt–^{1}H spin coupling constants, which vary from about 10 to 60 Hz in Pt–N–C–H fragments, is suggested by the data. Simultaneous determination of J_{Pt-H} and J_{H-H} in several of the complexes indicates that J_{Pt-H} for Pt–N–C–H fragments is a maximum for dihedral angles (ϕ) near 180° and approaches a minimum for $\phi = 0°$. This conclusion is used to determine preferred conformations of other coordinated ligands.

As part of a study of stable diamagnetic complexes of nitrogen- and sulfur-containing ligands, we have synthesized several amino acid complexes of Pt(II) and have analyzed their proton nmr spectra. This paper (I) describes syntheses and analyses of proton nmr spectra of several of these complexes and discusses the ligand conformations which these data reveal. Separate papers describe subsequent studies of the kinetics of proton exchange and racemization of several complexes (II)[5] and the kinetics of inversion through sulfur in several complexes of S-methyl-L-cysteine (III).[6]

Structural formulas of the anion forms of the amino acids whose Pt(II) complexes (**1-6**) are described in this paper are given in Chart I. These particular compounds were chosen to represent a series of increasing complexity ranging from simple amino acids capable of N coordination or N, O chelation to compounds capable of forming a variety of complex species involving combinations of oxygen, nitrogen, and sulfur coordination.[7]

Chart I



1, R_1–R_4 = H and CH_3 in five combinations

2

3, $n = 1, 2$

4

5

6, $n = 1, 2$; $R = CH_3, C_2H_5$

Several proton nmr studies of protonation sites and/or rotational conformations of these and similar amino acids have been reported.[8] Previously studied metal complexes of these amino acids range from labile[9]

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(1) Portions of this work were reported at the 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1965, and the 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967.

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(3) National Science Foundation Undergraduate Research Participant, Summer 1966.

(4) National Science Foundation Undergraduate Research Participant, Summer 1965.

(5) L. E. Erickson, A. Dappen, H. Fritz, R. May, J. Uhlenhopp, and D. Wright, in preparation.

(6) L. E. Erickson and J. McDonald, in preparation.

(7) The following abbreviations will be used through this paper: glycinate = Gly^-, glycine·HCl = H_2Gly^+, glycine = HGly, etc.; alanine = HAla; sarcosine = HSar; α-aminoisobutyric acid = HAbu; N,N-dimethylglycine = HDmg; α,β-diaminopropionate = Dap^-; aspartate = Asp^{2-}; glutamate = Glu^{2-}; histidine = HHist; S-methylcysteine = HS-MeCys; methionine = HMet; S-ethylcysteine = HS-EtCys.

(8) (a) A. Nakamura and N. K. Zasshi, *J. Chem. Soc. Japan*, **86**, 780 (1965); (b) R. B. Martin and R. Mathur, *J. Am. Chem. Soc.*, **87**, 1065 (1965); (c) J. A. Glasel, *ibid.*, **87**, 5472 (1965); (d) K. G. R. Pachler, *Z. Anal. Chem.*, **224**, 211 (1966); (e) C. C. J. Calvenor and N. S. Ham, *Chem. Commun.*, 537 (1966); (f) J. R. Cavanaugh, *J. Am. Chem. Soc.*, **89**, 1558 (1967).

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