

Role of the Bridging Ligand in Inner-Sphere Electron-Transfer Reactions

Albert Haim

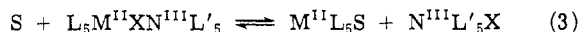
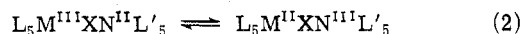
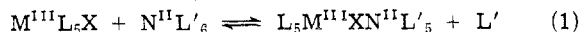
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Some redox reactions between metal complexes in solution are known as *inner-sphere* reactions. They are characterized by the formation of a binuclear complex (an intermediate and/or a transition state) along the redox pathway between reactants and products. A central feature of the binuclear complexes is a ligand, known as the bridging ligand,¹ that forms part of the coordination spheres of both the oxidizing and the reducing metal ions.

A contrasting category is that of *outer-sphere* reactions in which an electron appears to be transferred directly from one complex to the other, without interpenetration of the coordination shells of the metal ions.

The direct demonstration of the inner-sphere mechanism is based, in major part, on ligand-transfer studies,²⁻⁴ but the detection of binuclear intermediates in which the metals exhibit the initial⁵⁻⁷ or the final oxidation states⁸⁻¹¹ has also provided important information. The elementary steps in the pathway connecting reactants to products are usually represented as in eq 1-3.^{12,13}



Equation 1 is a substitutional step and results in the formation of the precursor binuclear complex where the two metal ions are bridged by the ligand X. Activation of the precursor complex results in a configuration appropriate for electron transfer. Transfer takes place under Franck-Condon restrictions, and is followed by deactivation with formation of the successor¹² or postcursor¹⁴ complex. Finally, the successor binuclear complex dissociates into mononuclear products, and the overall redox reaction is consummated.

When reaction 1 or 3 is rate determining, the overall process is substitution controlled. When the rate-determining step is reaction 2, it is electron transfer controlled. The faster vanadium(II) reductions of carboxylatoamminecobalt(III) complexes are examples of substitution-controlled redox reactions with eq 1 rate determining.¹⁵⁻¹⁷ The chromium(II) reductions of some chlororuthenium(III) complexes fea-

ture eq 3 as the rate-determining step.^{9,10}

In the present Account, we are concerned with the role of the bridging ligand in electron-transfer reactions, and therefore focus attention on those systems for which eq 2 controls the reaction rate.

Effect of Hydrogen Ion Concentration on Reaction Rates

Unless there is strong association between the reactants,^{5,6,18} most one-electron redox reactions between metal complexes follow mixed second-order kinetics. External anions, e.g., those not included in the coordination spheres of the metal ions, often affect reaction rates, but such effects are not considered here, and the reader is referred to the most recent review on this subject.¹⁹ The only external reagent affecting reaction rates that is of importance in the present discussion is the hydrogen ion.

Can Water Serve as a Bridging Ligand? When the dominant form of one of the reactants is present as a protonated form, parallel acid-independent and inverse acid paths are often encountered. Thus, the $\text{Co}(\text{NH}_3)_5\text{OH}_2^{3+}-\text{Cr}^+$ reaction in a sodium perchlorate medium obeys the rate law²⁰

$$(k_0 + k_{-1}/[\text{H}^+])[\text{Co}(\text{NH}_3)_5\text{OH}_2^{3+}][\text{Cr}^{2+}] \quad (4)$$

which is interpreted as two parallel pathways with activated complexes of composition $[\text{CrCo}(\text{NH}_3)_5\text{OH}_2^{5+}]^\ddagger$ and $[\text{CrCo}(\text{NH}_3)_5\text{OH}_4^{4+}]^\ddagger$. However, from a reexamination²¹ of this system using lithium perchlorate, it was concluded that the k_0 term is, most probably, the manifestation of a medium effect.

(1) H. Taube, H. Myers, and R. L. Rich, *J. Am. Chem. Soc.*, **75**, 4118 (1953).

(2) H. Taube, *Adv. Inorg. Chem. Radiochem.*, **1**, 1 (1959).

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

(4) A. Haim and N. Sutin, *J. Am. Chem. Soc.*, **88**, 5343 (1966).

(5) R. D. Cannon and H. Gardiner, *J. Am. Chem. Soc.*, **92**, 3800 (1970).

(6) R. D. Cannon and A. Gardiner, *Inorg. Chem.*, **13**, 390 (1974).

(7) E. S. Gould, *J. Am. Chem. Soc.*, **94**, 4360 (1972).

(8) A. Haim and W. K. Wilmarth, *J. Am. Chem. Soc.*, **83**, 509 (1961).

(9) W. G. Movius and R. G. Linck, *J. Am. Chem. Soc.*, **91**, 5394 (1969).

(10) D. Seewald, N. Sutin, and K. O. Watkins, *J. Am. Chem. Soc.*, **91**, 7307 (1969).

(11) B. Grossman and A. Haim, *J. Am. Chem. Soc.*, **92**, 4835 (1970).

(12) N. Sutin, *Acc. Chem. Res.*, **1**, 225 (1968).

(13) It is assumed that N^{II} accepts substitution more readily than M^{III} , whereas the reverse situation obtains for N^{III} and M^{II} .

(14) R. G. Linck, *MPT Int. Rev. Sci., Inorg. Chem., Ser. One*, **9**, 303 (1971).

(15) H. J. Price and H. Taube, *Inorg. Chem.*, **7**, 1 (1968).

(16) C. Hwang and A. Haim, *Inorg. Chem.*, **9**, 500 (1970).

(17) T. J. Przystas and A. Haim, *Inorg. Chem.*, **11**, 1016 (1972).

(18) D. Gaswick and A. Haim, *J. Am. Chem. Soc.*, **93**, 7347 (1971).

(19) J. E. Earley, *Prog. Inorg. Chem.*, **13**, 243 (1970).

(20) A. Zwickel and H. Taube, *J. Am. Chem. Soc.*, **81**, 1288 (1959).

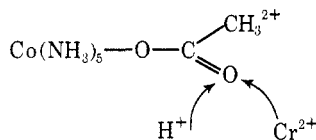
(21) D. T. Toppen and R. G. Linck, *Inorg. Chem.*, **10**, 2635 (1971).

Albert Haim was born in France in 1931. He received the Industrial Chemistry degree in 1954 from the University of Uruguay, and the Ph.D. degree in 1960 from the University of Southern California where his research was directed by Wayne K. Wilmarth. After a postdoctoral year with Henry Taube at Stanford University, he joined The Pennsylvania State University and, in 1966, moved to the State University of New York at Stony Brook, where he is now Professor of Chemistry.

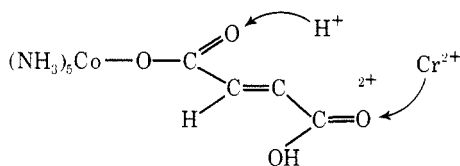
A similar conclusion had been previously reached in a study of the $\text{Fe}^{3+}\text{-Cr}^{2+}$ reaction²² in a lithium perchlorate medium.²³ Moreover, a reexamination²⁴ of the $\text{Cr}^{2+}\text{-Cr}^{3+}$ exchange reaction confirmed the earlier²⁵ upper limit of $2 \times 10^{-5} \text{ M}^{-1} \text{ sec}^{-1}$ for the acid-independent term.

On the basis of this information, it was suggested²¹ that water does not act as a bridging ligand in reductions by Cr^{2+} . In view of the extremely low basicity of coordinated water, it seems unlikely that it can serve as a bridging ligand in other redox reactions. Therefore, we suggest that, if water is the only potential bridging ligand, an acid-independent term in the rate law corresponds to an outer-sphere pathway. Support for this hypothesis is obtained from isotope fractionation studies and the effect of external anions on the $\text{Co}(\text{NH}_3)_5\text{OH}_2^{3+}\text{-V}^{2+}$ reaction,²⁶ and from comparisons of the $\text{Co}(\text{NH}_3)_5\text{OH}_2^{3+}\text{-Eu}^{2+}$ reaction with known outer-sphere reactions.²⁷

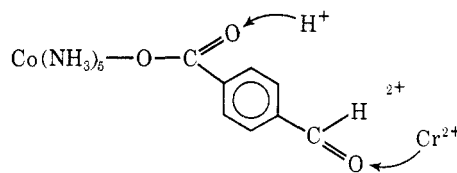
What Are the Consequences of Protonation of the Bridging Ligand? Complexes with ligands containing basic sites can exhibit either rate acceleration or retardation with increasing hydrogen ion concentration. The rate retardation found in the chromium(II)²⁸ and vanadium(II)¹⁷ reductions of *cis*- $\text{Co}(\text{en})_2(\text{HCO}_2)_2^+$ and in the $\text{Co}(\text{NH}_3)_5\text{OCOCH}_3^{2+}\text{-Cr}^{2+}$ reaction²⁹ is interpreted as an equilibrium effect, hydrogen ion and the reducing agent competing for the same site (presumably the carbonyl oxygen) in the bridging ligand. Rate acceleration is found in the



chromium(II) reductions of fumaratopentaammincobalt(III)³⁰ and *p*-formylbenzoatopentaammincobalt(III).³¹ In the former case, improved conjugation between the two metal centers upon protonation of the adjacent carbonyl oxygen is invoked (remote attack with resonance transfer).

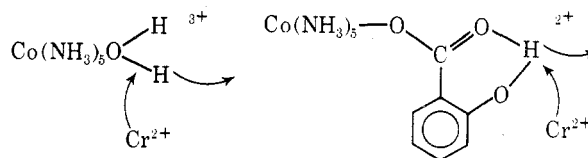


In the second case, chromium(II) is known to attack the formyl oxygen, and it is postulated that protonation of the adjacent carbonyl oxygen lowers the energy of the unoccupied ligand orbital that accepts the electron (remote attack with chemical or stepwise mechanism).



Finally, medium effects can manifest themselves as changing rates with changing hydrogen ion concentration, giving rise to apparent acid-dependent pathways; therefore, utmost care must be exercised in choosing ionic media to control ionic strength.^{32,33}

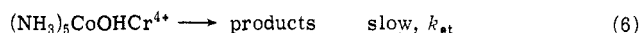
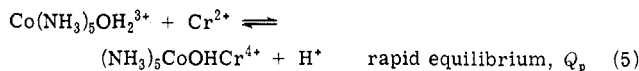
Mechanistic Ambiguities for Inverse Acid Pathways. The chromium(II) reductions of aquopentaammincobalt(III) and salicylatopentaammincobalt(III) feature an inverse acid term in the rate laws. The mechanistic implication is that removal of a proton provides a favorable pathway for formation of the precursor binuclear complex. However, there



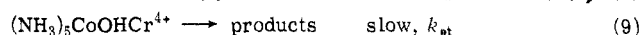
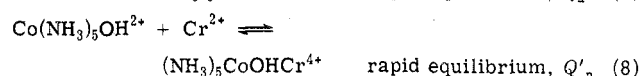
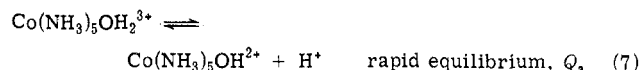
are mechanistic ambiguities associated with these pathways, and the two systems (which have been incorrectly discussed in the literature) will be used to illustrate the problems involved.^{14,34}

Two mechanisms,³⁵ A and B, can be formulated for the $1/[\text{H}^+]$ pathway of the $\text{Co}(\text{NH}_3)_5\text{OH}_2^{3+}\text{-Cr}^{2+}$ reaction. The value of k_{-1} (see eq 4) is interpreted as¹

Mechanism A



Mechanism B



$Q_p k_{et}$ in mechanism A and as $Q_a Q'_p k_{et}$ in mechanism B. The ambiguity arises because, in both mechanisms, the steps preceding the rate-determining electron transfer are rapid equilibria. Under these circumstances, the rate law specifies the composition of the activated complex, but not the order of aggregation and/or dissociation of the species that produce it.³⁶⁻³⁸ The two mechanisms are depicted diagrammatically in Figure 1. It has been argued¹⁴ that, if dissociation of the proton does not obtain and mechanism A is operative, then dividing k_{-1} by Q_a leads

(22) G. Dulz and N. Sutin, *J. Am. Chem. Soc.*, **86**, 829 (1964).

(23) D. W. Carlyle and J. H. Espenson, *J. Am. Chem. Soc.*, **91**, 599 (1969).

(24) E. Deutsch and H. Taube, *Inorg. Chem.*, **7**, 1532 (1968).

(25) A. Anderson and N. A. Bonner, *J. Am. Chem. Soc.*, **76**, 3826 (1954).

(26) H. Diebler, P. Dodel, and H. Taube, *Inorg. Chem.*, **5**, 1688 (1966); P. Dodel and H. Taube, *Z. Phys. Chem. (Frankfurt am Main)*, **44**, 92 (1965).

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

(28) J. R. Ward and A. Haim, *J. Am. Chem. Soc.*, **92**, 475 (1970).

(29) M. B. Barrett, J. H. Swinehart, and H. Taube, *Inorg. Chem.*, **10**, 1983 (1971).

(30) H. Diaz and H. Taube, *Inorg. Chem.*, **9**, 1304 (1970), and references therein.

(31) A. Zanella and H. Taube, *J. Am. Chem. Soc.*, **94**, 6403 (1972).

(32) T. W. Newton and B. B. Baker, *J. Phys. Chem.*, **67**, 1425 (1963).

(33) C. Lavalley and E. Deutsch, *Inorg. Chem.*, **11**, 3133 (1972).

(34) A. Liang and E. S. Gould, *J. Am. Chem. Soc.*, **92**, 6791 (1970).

(35) A third mechanism¹⁴ involving preequilibrium formation of a water-bridged binuclear complex is neglected on the basis of our discussion (vide supra) of the unlikely role of water as a bridging ligand.

(36) E. L. King in "Catalysis", P. H. Emmett, Ed., Vol. II, Reinhold, New York, N.Y., 1955, p 337.

(37) T. W. Newton and F. B. Baker, *Adv. Chem. Ser.*, No. 71, 268 (1967).

(38) A. Haim, *Inorg. Chem.*, **5**, 2081 (1966).

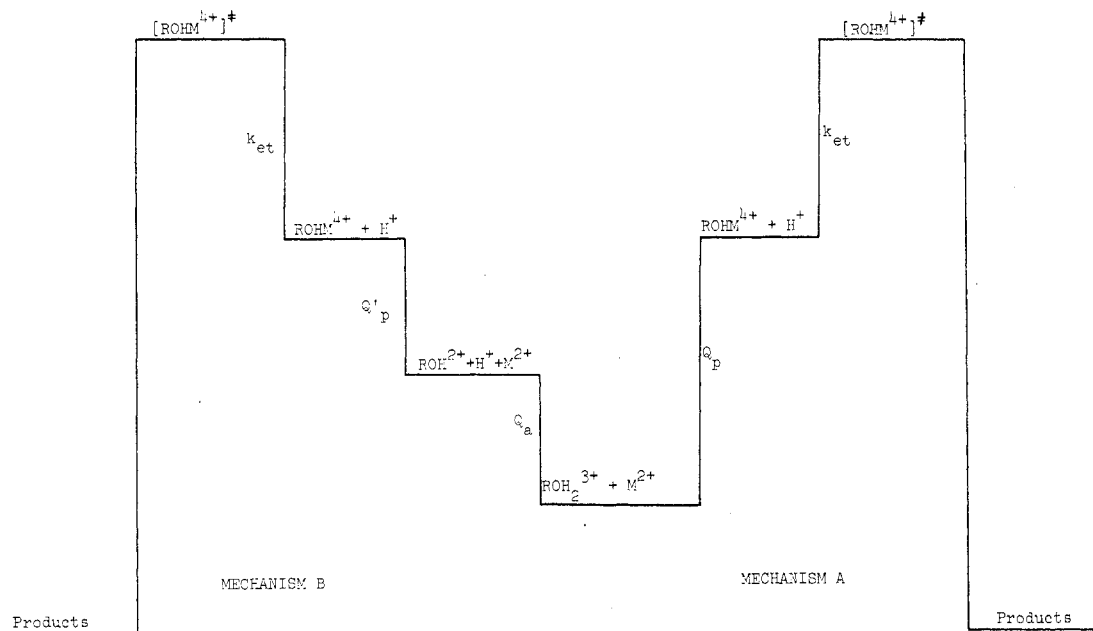
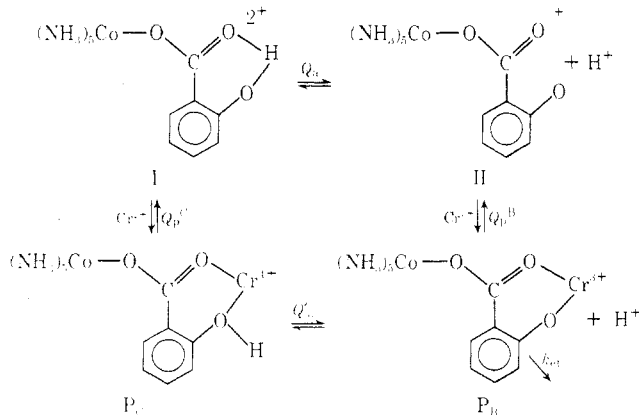


Figure 1. Free-energy profile for Mechanisms A and B for the reaction $\text{Co}(\text{NH}_3)_5\text{OH}_2^{3+} + \text{Cr}^{2+}$ ($\text{R} = \text{Co}(\text{NH}_3)_5$, $\text{M} = \text{Cr}$).

to a fictitious value of a second-order rate constant ($Q_p k_{et}/Q_a$) which would, in turn, lead to incorrect comparisons with genuine second-order rate constants (say for the $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+} - \text{Cr}^{2+}$ reaction). This argument is correct provided that proton dissociation according to eq 7 is precluded.

However, the proton-transfer reactions of aquo complexes are rapid and reversible and *all* the species involved in reactions prior to the electron transfer are in equilibrium. Consequently, whether the precursor complex $(\text{NH}_3)_5\text{CoOHCr}^{4+}$ is formed predominantly by reaction 5, by reaction 8, or by comparable contributions from the two reactions, it is perfectly meaningful to inquire (and make comparisons) about the free-energy difference between $\text{Co}(\text{NH}_3)_5\text{OH}^{2+} + \text{Cr}^{2+}$ and the transition state $[(\text{NH}_3)_5\text{CoOHCr}^{4+}]^\ddagger$.

In the case of the salicylatopentaamminecobalt(III)-chromium(II) reaction, the precursor complex P_B can be formed either by reaction between the deprotonated complex II and chromium(II) or by pro-

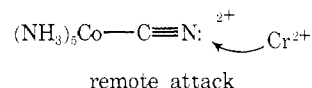


ton dissociation from the precursor complex P_C . In the former case, $k_{-1} = Q_a Q_p^B k_{et}$, and in the latter case, $k_{-1} = Q_p^C Q_a k_{et}$. Using $k_{-1} = 0.03 \text{ sec}^{-1}$ and $pQ_a = 10.2$,³⁴ then $Q_p^B k_{et} = 4.80 \times 10^8 \text{ M}^{-1} \text{ sec}^{-1}$. Since this value is higher, by several orders of magni-

tude, than second-order rate constants for chromium(II) reductions of other carboxylato complexes and approaches the value for a diffusion-controlled reaction, it was concluded³⁴ that P_B was formed by proton loss from P_C rather than by association between II and Cr^{2+} . But since I, II, and P_C are connected by rapid equilibria, it is apparent that, in order to preclude a rapid equilibrium between II, Cr^{2+} , and P_B , a barrier for substitution into Cr^{2+} by II must exist. However, there appears to be no electronic or geometric feature in II to prevent rapid substitution into the coordination sphere of Cr^{2+} , especially in view of the postulated rapid substitution by I. Therefore, provided that the acid-base and chromium(II) substitution equilibria are rapid³⁹ compared to electron transfer, this system is completely analogous to the $\text{Co}(\text{NH}_3)_5\text{OH}_2^{3+} - \text{Cr}^{2+}$ system.

Geometric Considerations. Adjacent and Remote Attacks, Doubly Bridging, Chelation

Early in the development of the field, there was interest in determining the sites used by the bridging ligand to bind the two metal ions. For example, in the reduction of cyanoamminecobalt(III) complexes by chromium(II),⁴⁰ the only available lone pair is on the nitrogen atom of CN^- , and consequently, bridging occurs as shown. On the other hand, for an oxidant



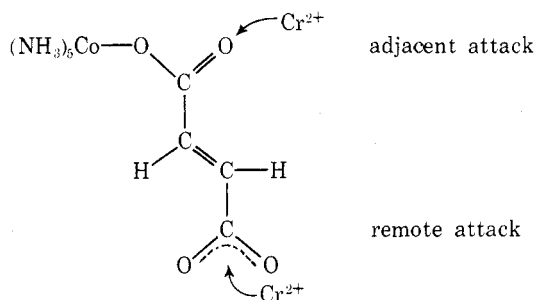
such as fumaratopentaamminecobalt(III), the reductant can bind either the oxygen atom near the cobalt(III) center or one of the oxygen atoms of the carboxylate group far from the cobalt.⁴¹ Attack by the

(39) It may be, however, that the equilibria involving I are not rapidly established. A. C. Dash and R. K. Nanda, *Inorg. Chem.*, 12 2024 (1973), report that the reaction of I with Al^{3+} to produce $(\text{NH}_3)_5\text{CoOCOC}_6\text{H}_4\text{OAl}^{4+}$ reaches completion in approximately 10 min at 28°.

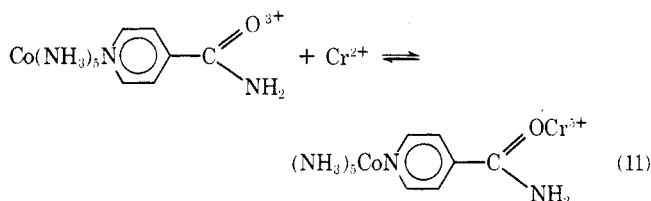
(40) J. P. Birk and J. H. Espenson, *J. Am. Chem. Soc.*, 90, 1153 (1968).

(41) Attack at the oxygen atom bound to the cobalt has been shown to be inoperative: K. L. Scott and A. G. Sykes, *J. Chem. Soc., Dalton Trans.*, 1832 (1972).

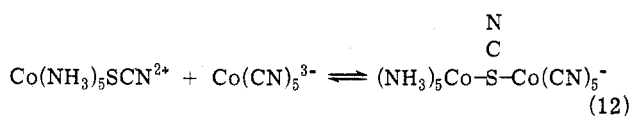
reducing agent at the lead-in atom of the bridging ligand or, in the case of carboxylate complexes, at the carbonyl oxygen nearest the oxidizing center is referred to as *adjacent*.⁴² The term *remote* attack denotes binding by the reductant at any other site.



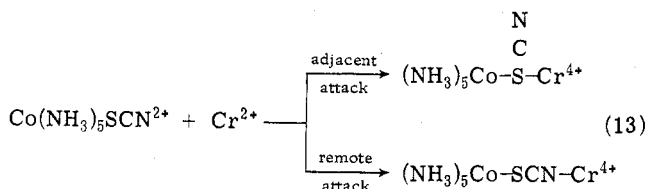
Evidently, monoatomic ligands can only display adjacent attack. For polyatomic ligands, remote attack provides a fairly common reaction pathway. Thus, chromium(II) reacts with isothiocyanatopentaamminecobalt(III)⁴³ and isonicotinamidopentaamminecobalt(III)⁴⁴ by remote attack (eq 10 and 11).



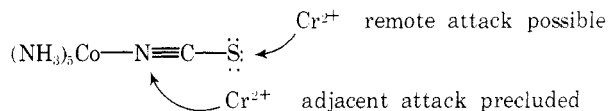
Only two firmly established examples of adjacent attack at the lead-in atom have been reported. The reduction of $\text{Co}(\text{NH}_3)_5\text{SCN}^{2+}$ by $\text{Co}(\text{CN})_5^{3-}$ proceeds exclusively *via* adjacent attack (eq 12)⁴⁵ and reduc-



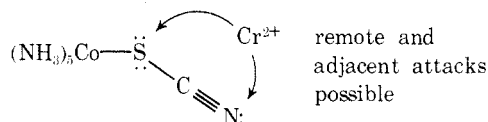
tion by Cr^{2+} features parallel adjacent and remote pathways (eq 13).⁴³



The contrasting behavior between the isothiocyanate (only remote attack) and thiocyanate (at least some adjacent attack) complexes can be rationalized on the basis of the electronic structures. The Co-N-C bond in $[\text{Co}(\text{NH}_3)_5\text{NCS}]\text{Cl}_2$ is linear.⁴⁶ Therefore, a pair of electrons is not available for reaction via adjacent attack, and reaction proceeds via remote attack at sulfur. For the thiocyanato complex, both the sul-

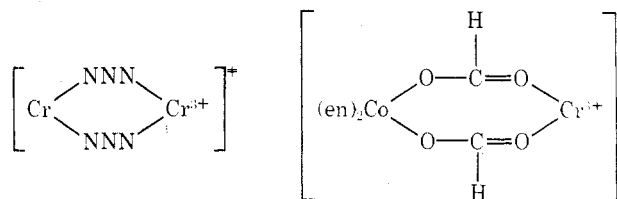


fur and nitrogen atoms have a lone pair available, and it is not unexpected that parallel adjacent and remote attacks by chromium(II) obtain. The aston-

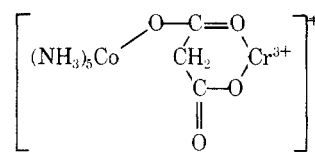


ishing feature, however, is the efficiency of the reaction for attack at sulfur ($k = 8.0 \times 10^4 \text{ M}^{-1} \text{ sec}^{-1}$ compared to $1.9 \times 10^5 \text{ M}^{-1} \text{ sec}^{-1}$ for attack at nitrogen). On the basis of thermodynamic and steric factors,⁴³ a value of 10^3 for the ratio of remote to adjacent attacks by Cr^{2+} on $\text{Co}(\text{NH}_3)_5\text{SCN}^{2+}$ is a reasonable estimate. The observed ratio 2.4 is substantially smaller, and, therefore, since the rate of remote attack seems to be in line with rates of reactions of similar compounds (k for $\text{Co}(\text{NH}_3)_5\text{N}_3^{2+} + \text{Cr}^{2+}$ is $3 \times 10^5 \text{ M}^{-1} \text{ sec}^{-1}$), it appears that an unusually high reactivity is associated with adjacent attack by Cr^{2+} on $\text{Co}(\text{NH}_3)_5\text{SCN}^{2+}$. The high electron-mediating ability of sulfur bound to cobalt(III) has been observed in other Co(III)-Cr(II) systems,⁴⁷ but the factor or factors responsible for the high rates are not apparent.

In the reactions of *cis*- $\text{Cr}(\text{N}_3)_2^+$, *cis*- $\text{Co}(\text{NH}_3)_4(\text{N}_3)_2^8$, and *cis*- $\text{Co}(\text{en})_2(\text{HCO}_2)_2^+$ with Cr^{2+} ,^{28,48,49} two ligands are transferred from oxidant to reductant, and it is inferred that doubly bridged transition states are involved. In the reduction of



malonatopentaamminecobalt(III) by Cr^{2+} ,^{33,50} the kinetically controlled product is the chelated malonatochromium(III) complex,⁵¹ and therefore chelation obtains in the transition state. These effects are ac-



companied by considerable increases in rates,^{28,50} presumably because of the increased stability of the precursor complexes. Additional geometric details about precursor complexes or transition states are lacking. Thus, it is not known whether the Co-Cl-Cr bond is linear or not in the transition state for the most famous inner-sphere reaction ($\text{Co}(\text{NH}_3)_5\text{Cl}^{2+} + \text{Cr}^{2+}$), although both linear⁵² and angular⁵³ halide

(42) The designation adjacent attack for reaction at the carbonyl oxygen near the oxidant is inconsistent with the designation used for ligands other than carboxylate. This admittedly arbitrary definition is widely used because of historical reasons.²

(43) C. Shea and A. Haim, *J. Am. Chem. Soc.*, **93**, 3055 (1971).

(44) F. Nordmeyer and H. Taube, *J. Am. Chem. Soc.*, **90**, 1162 (1968).

(45) C. Shea and A. Haim, *Inorg. Chem.*, **12**, 3013 (1973).

(46) M. R. Snow and R. F. Boomsma, *Acta Crystallogr., Sect. B*, **28**, 1908 (1972).

(47) R. H. Lane and L. E. Bennett, *J. Am. Chem. Soc.*, **92**, 1089 (1970).

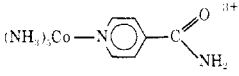
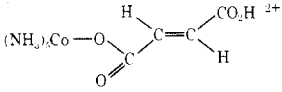
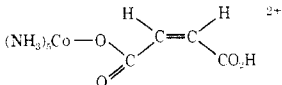
(48) R. Snellgrove and E. L. King, *J. Am. Chem. Soc.*, **84**, 4609 (1962).

(49) A. Haim, *J. Am. Chem. Soc.*, **88**, 2324 (1966).

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

(51) D. Huchital and H. Taube, *Inorg. Chem.*, **4**, 1660 (1965); M. V. Olson and C. E. Behnke, *ibid.*, **13**, 1329 (1974).

Table I
Rate Constants for Selected Reactions of Cr(II) with
Co(III) and Cr(III) Complexes (25°, $\mu = 1.0 M$)

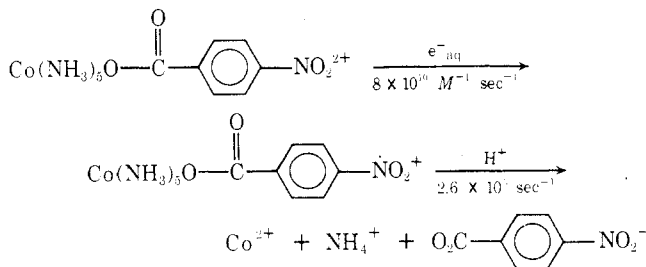
Oxidant	$k, M^{-1} \text{ sec}^{-1}$	$k_{\text{Co}(\text{NH}_3)_5\text{L}} / k_{\text{Cr}(\text{H}_2\text{O})_5\text{L}}$
$(\text{NH}_3)_5\text{CoNCS}^{2+}$	19	1.4×10^5
$(\text{NH}_3)_5\text{CoF}^{2+}$	9×10^5	3.4×10^7
$(\text{NH}_3)_5\text{CoOH}^{2+}$	1.6×10^6	2.3×10^6
	17.4	10
	1.32	0.4
	2×10^2	50

bridges have been substantiated by X-ray diffraction studies of stable binuclear complexes.

Chemical Mechanism. Direct Participation of Bridging Ligand

Following the activation of the precursor binuclear complex, electron transfer takes place. Two extreme roles can be envisaged for the bridging ligand.⁵⁴ The electron (or hole) can be transferred to the ligand, and, in a subsequent step, from the ligand radical intermediate to the oxidizing center (or reducing center). Alternately, at no time is the electron (or hole) in a bound state of the ligand, and the bridge acts simply as a mediator. The mechanistic designations for the two cases are chemical, radical or stepwise mechanism and resonance or exchange mechanism, respectively.

Generation of Bound Radical by Pulse Radiolysis. Evidence for the direct participation of ligands comes from pulse radiolytic studies of *p*-nitrobenzoatopentaamminecobalt(III). Hydrated electrons react rapidly with the complex and a metastable intermediate, which decays by a first-order process to cobalt(II), is produced.⁵⁵ The intermediate is assumed to be the cobalt(III) complex of the radical ion derived by reduction of the ligand, and the first-order decay corresponds to intramolecular electron transfer from the radical to the cobalt(III) center.



Indirect Criterion for Chemical Mechanism. Since coordinated radicals are elusive intermediates,

(52) D. Baumann, H. Endres, H. J. Keller, and J. Weiss, *J. Chem. Soc., Chem. Commun.*, 853 (1973).

(53) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", 3rd ed, Interscience, New York, N.Y., 1972, p 468.

(54) P. George and J. Griffith in "The Enzymes", P. Boyer, Ed., Vol. I, Academic Press, New York, N.Y. 1959, p 347.

(55) M. Z. Hoffman and M. Simic, *J. Am. Chem. Soc.*, **94**, 1757 (1972).

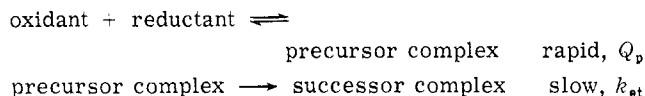
an indirect criterion has been developed to recognize the operation of a chemical mechanism.⁴² This involves comparisons of reductions of cobalt(III) and chromium(III) complexes with the same reductant and via the same bridging ligand. In the chemical mechanism, electron transfer takes place to the ligand, and, insofar as the ligand orbitals are not much affected by coordination, the rate of electron transfer to the ligand will be rather insensitive to the nature of the oxidant. Conversely, for the resonance mechanism, important changes in the inner coordination shell of the oxidant are part of the activation process, and rates will depend on the identity of the oxidant.

Some results are presented in Table I. In selected cases (F^- , OH^- , NCS^-), where thermodynamic arguments⁵⁶ rule out the chemical mechanism, rate ratios $k_{\text{CoA}_5\text{L}}/k_{\text{CrW}_5\text{L}}$ are in the range 10^5 – 10^7 . This is in accord with the expectation of strong discrimination in rate with respect to oxidizing center for the resonance mechanism. In contrast, the rate ratio for isonicotinamide as the bridging ligand is small (10), and it is inferred that the chemical mechanism obtains. Fumarate and maleate also give low $k_{\text{CoA}_5\text{L}}/k_{\text{CrW}_5\text{L}}$ ratios (0.4 and 50), and it was concluded^{30,57} that the radical mechanism is operative.

Although some reservations have been expressed in the use of rate ratios as a diagnostic of resonance vs. chemical mechanism,⁵⁸ and it is important to consider carefully the nature of the metal orbitals accepting the electron in making rate comparisons,⁵⁹ there is no question that the chemical mechanism provides an accessible and favorable pathway for electron transfer. In particular, when the electron must be transferred through long distances and there is mismatch in the symmetries of the donor, acceptor, and ligand orbitals, the distortions about the two metal centers needed to meet Franck–Condon restrictions may be uncoupled,⁶⁰ and the stepwise mechanism becomes preferred.

Resonance Mechanism. Thermodynamic and Kinetic Contributions to the Role of the Bridging Ligand

In the resonance exchange mechanism, the bridging ligand brings together the two metal centers and mediates the electron transfer. In trying to assess the role of the bridging ligand, one must decide what quantitative measurement will be used. Since we are concerned with reactivity, it seems appropriate to turn to rate constants. For simple inner-sphere reactions where the kinetics are mixed second order, the electron-transfer step is rate determining, and the resonance transfer mechanism obtains, the measured rate coefficient is the product of the equilibrium constant Q_p for precursor complex formation and the rate constant k_{et} for electron transfer within the binuclear unit. The role of the bridging ligand is there-



(56) H. Taube and E. S. Gould, *Acc. Chem. Res.*, **2**, 321 (1969).

(57) M. V. Olson and H. Taube, *Inorg. Chem.*, **9**, 2072 (1970).

(58) R. Davies and R. B. Jordan, *Inorg. Chem.*, **10**, 2432 (1971).

(59) R. G. Gaunter and H. Taube, *Inorg. Chem.*, **9**, 2627 (1970).

(60) H. Taube, *Pure Appl. Chem.*, **24**, 289 (1970).

Table II
Rate Constants, Equilibrium Constants and Intrinsic Barriers for Reactions of Azido and Thiocyanato Complexes that Proceed via Remote Attack (25°)

Reaction	$k_1, M^{-1} \text{ sec}^{-1}$	K	$k_{\text{intr}}, M^{-1} \text{ sec}^{-1}$
$\text{Co}(\text{NH}_3)_5\text{NCS}^{2+} + \text{Cr}^{2+} \rightleftharpoons \text{Co}(\text{NH}_3)_5^{2+} + \text{CrSCN}^{2+}$	19	5.2×10^4	8.3×10^{-2}
$\text{Co}(\text{NH}_3)_5\text{N}_3^{2+} + \text{Cr}^{2+} \rightleftharpoons \text{Co}(\text{NH}_3)_5^{2+} + \text{CrN}_3^{2+}$	3×10^5	3.7×10^{11}	0.49
$\text{Co}(\text{NH}_3)_5\text{SCN}^{2+} + \text{Cr}^{2+} \rightleftharpoons \text{Co}(\text{NH}_3)_5^{2+} + \text{CrNCS}^{2+}$	1.9×10^5	4.7×10^{15}	2.8×10^{-3}
$\text{Co}(\text{NH}_3)_5\text{NCS}^{2+} + \text{Fe}^{2+} \rightleftharpoons \text{Co}(\text{NH}_3)_5^{2+} + \text{FeSCN}^{2+}$	$<3 \times 10^{-6}$	6.4×10^{-16}	$<1.2 \times 10^2$
$\text{Co}(\text{NH}_3)_5\text{N}_3^{2+} + \text{Fe}^{2+} \rightleftharpoons \text{Co}(\text{NH}_3)_5^{2+} + \text{FeN}_3^{2+}$	8.8×10^{-3}	3.6×10^{-8}	46
$\text{Co}(\text{NH}_3)_5\text{SCN}^{2+} + \text{Fe}^{2+} \rightleftharpoons \text{Co}(\text{NH}_3)_5^{2+} + \text{FeNCS}^{2+}$	0.12	5.8×10^{-5}	15.8
$\text{Cr}(\text{OH}_2)_5\text{NCS}^{2+} + \text{Cr}^{2+} \rightleftharpoons \text{Cr}^{2+} + \text{Cr}(\text{OH}_2)_5\text{SCN}^{2+}$	1.4×10^{-4}	3.3×10^{-6}	7.5×10^{-2}
$\text{Cr}(\text{OH}_2)_5\text{N}_3^{2+} + \text{Cr}^{2+} \rightleftharpoons \text{Cr}^{2+} + \text{Cr}(\text{OH}_2)_5\text{N}_3^{2+}$	6	1	6
$\text{Cr}(\text{OH}_2)_5\text{SCN}^{2+} + \text{Cr}^{2+} \rightleftharpoons \text{Cr}^{2+} + \text{Cr}(\text{OH}_2)_5\text{NCS}^{2+}$	40	3.0×10^5	7.5×10^{-2}

fore dual. It brings the metal ions together (thermodynamic contribution) and mediates the transfer of the electron (kinetic contribution). The thermodynamic effect can be understood on the basis of the usual considerations about stability constants of complexes. The kinetic effect manifests itself in the reorganization energy, the interaction energy, and the symmetry properties of donor, carrier, and acceptor orbital.^{60,61}

A somewhat different approach is based on the linear-free-energy relationship between rate constants and equilibrium constants. The efficiency of bridging ligands is measured by the intrinsic barrier to electron transfer obtained by correcting observed rate constants for the overall free energy of reaction.¹²

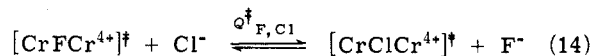
A third approach makes use of stability constants and rate constants to obtain relative stabilities of transition states.⁶² Effectively, this approach corrects the rate constants for differences in stabilities between the reactants.

Symmetrical and Unsymmetrical Bridging Ligands. Azide and Thiocyanate. Importance of Precursor Complex Stability. The reductions of $\text{Co}(\text{NH}_3)_5\text{N}_3^{2+}$ by Cr^{2+} ⁶³ or Fe^{2+} ⁶⁴ are considerably faster than the corresponding reductions of $\text{Co}(\text{NH}_3)_5\text{NCS}^{2+}$.^{63,65} Similarly, the exchange of chromium between CrN_3^{2+} and Cr^{2+} is considerably faster than the corresponding exchange reaction of CrNCS^{2+} .^{66,67} In these systems, both for reactants and for products, the nitrogen-bonded isothiocyanato complexes are the more stable linkage isomers. The early interpretation of the kinetic results (see Table II) was that the reactions proceed by inner-sphere remote attack and produce the thermodynamically unstable sulfur-bonded thiocyanato product and the stable nitrogen-bonded (by necessity) azido complex. The difference in the thermodynamic stability of the products was then invoked to account for the slow reactions of the isothiocyanato vs. the azido complexes.

This argument can be placed on a quantitative basis and shown⁶⁸ to be insufficient to account for

the trends. Rate constants for reactions with different overall standard free-energy changes can be corrected to obtain the intrinsic barrier¹² $k_{\text{intr}} = k/K^{1/2}$, where k is the observed rate constant and K the equilibrium constant for the reaction. The values obtained, included in Table II, show that in every case the corrected azide-mediated reactions are faster than those mediated by thiocyanate. Since equal intrinsic barriers would have been predicted from the simple thermodynamic argument, additional factors must be operative, and it was suggested that the differences in the stabilities of the precursor complexes can account for the trends.⁶⁸ Since $k = Q_p k_{\text{et}}$ and $k_{\text{intr}} = k/K^{1/2}$, it can be shown⁶⁸ that $k_{\text{intr}}^{\text{N}_3}/k_{\text{intr}}^{\text{SCN}} = Q_p^{\text{N}_3}/(Q_p^{\text{NCS}}Q_p^{\text{SCN}})^{1/2}$ and $k_{\text{intr}}^{\text{N}_3}/k_{\text{intr}}^{\text{NCS}} = Q_p^{\text{N}_3}/(Q_p^{\text{NCS}}Q_p^{\text{SCN}})^{1/2}$, where Q_p^{L} represents the equilibrium constant for formation of the precursor complex bridged by L. Since Cr^{2+} is a hard acid, it displays a strong discrimination in favor of binding nitrogen over sulfur. Therefore, $Q_p^{\text{N}_3}/(Q_p^{\text{NCS}}Q_p^{\text{SCN}})^{1/2} > 1$, and the intrinsic rate constants for azide acting as a bridge are larger than the corresponding constants for thiocyanate or isothiocyanate.

Reactions of Halogen Complexes. "Normal" and "Inverted" Orders. Relative Stabilities of Transition States. Because of historical reasons, the reactivity pattern $\text{I}^- > \text{Br}^- > \text{Cl}^- > \text{F}^-$ is referred to as "normal", whereas the opposite trend is called "inverted" or "reverse". For the reductions of $\text{Co}(\text{NH}_3)_5\text{X}^{2+}$, $\text{Cr}(\text{NH}_3)_5\text{X}^{2+}$, and $\text{Cr}(\text{H}_2\text{O})_5\text{X}^{2+}$ complexes (X is a halogen) by Cr^{2+} , the normal order is observed.⁶² For the reductions of $\text{Co}(\text{NH}_3)_5\text{X}^{2+}$ by Fe^{2+} and Eu^{2+} and of $\text{Ru}(\text{NH}_3)_5\text{X}^{2+}$ by Cr^{2+} , the reverse order obtains.⁶⁹ These trends are based on comparisons of second-order rate constants. A different approach for comparing a series of reactions uses relative stabilities of transition states.⁶² Thus, a useful quantity in comparing the $\text{CrCl}^{2+}-\text{Cr}^{2+}$ and $\text{CrF}^{2+}-\text{Cr}^{2+}$ reactions is the "equilibrium quotient" $Q_{\text{F,Cl}}^\ddagger$ for the reaction



The value of $Q_{\text{F,Cl}}^\ddagger$ can be computed as $k_{\text{Cl}}Q_{\text{Cl}}/$

(61) N. Sutin in "Inorganic Biochemistry", G. L. Eichhorn, Ed., Vol. 2, Elsevier, Amsterdam, 1973, p 611.

(62) A. Haim, *Inorg. Chem.*, **7**, 1475 (1968).

(63) J. P. Candlin, J. Halpern, and D. L. Trimm, *J. Am. Chem. Soc.*, **86**, 1019 (1964).

(64) A. Haim, *J. Am. Chem. Soc.*, **85**, 1016 (1963).

(65) J. Espenson, *Inorg. Chem.*, **4**, 121 (1965).

(66) D. L. Ball and E. L. King, *J. Am. Chem. Soc.*, **80**, 1091 (1958).

(67) R. Snellgrove and E. L. King, *Inorg. Chem.*, **3**, 288 (1964).

(68) D. P. Fay and N. Sutin, *Inorg. Chem.*, **9**, 1291 (1970). Note that in this article both k and k_{et} are taken to be proportional to $K^{1/2}$.

(69) H. Taube, "Electron Transfer Reactions of Complex Ions in Solution", Academic Press, New York, N.Y., 1970, p 51.

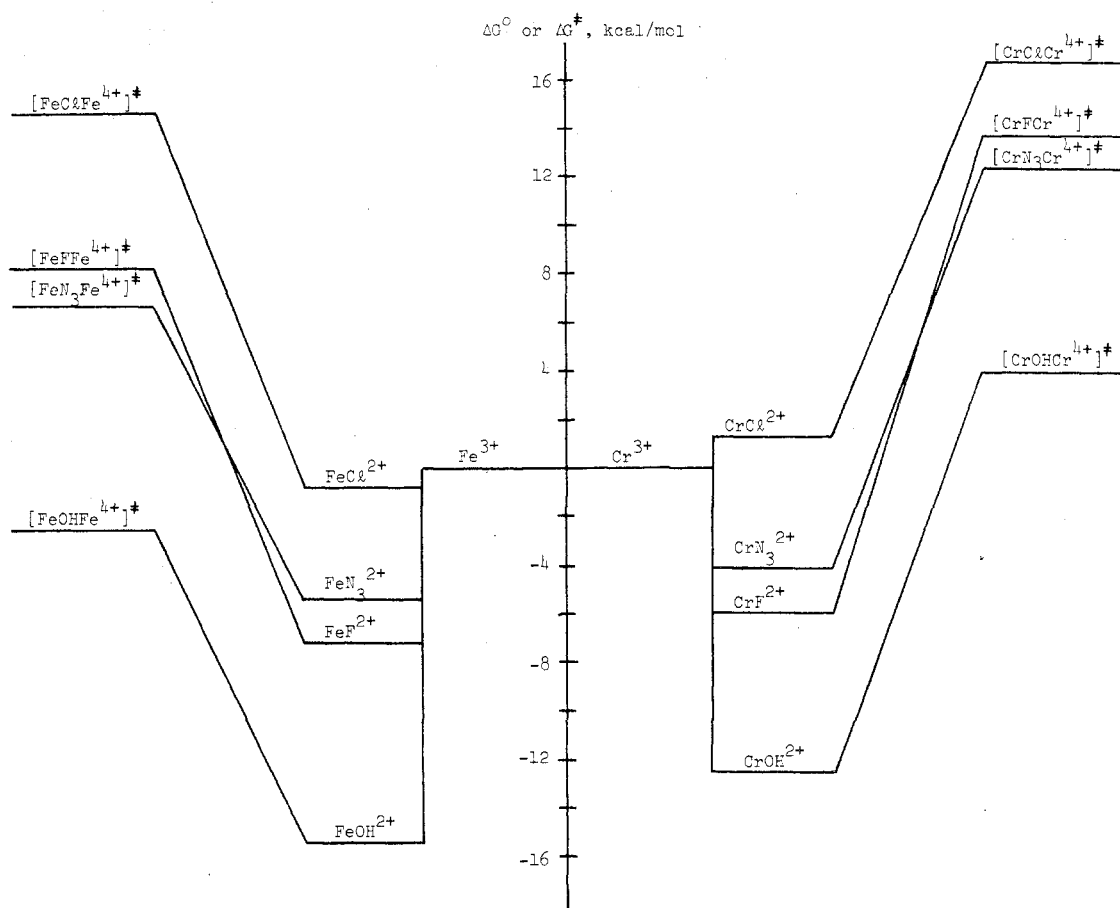
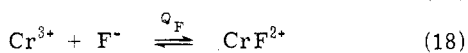
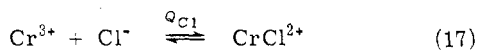
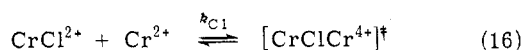
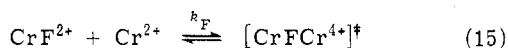
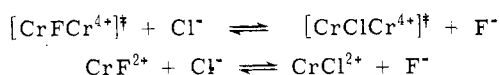


Figure 2. Relative stabilities of chromium and iron complexes and transition states.

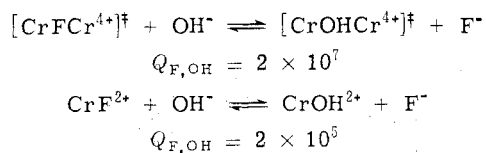
$k_F Q_F$ from



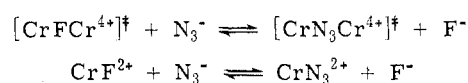
Effectively, values of $Q_{X,Y}^\ddagger$ provide a correction of the rate constant ratio k_X/k_Y for the difference in free energies of the ground states, and thus are a measure of the relative affinities of transition states for the bridging ligands X and Y.^{62,69} For example, the equilibrium quotients for



are 6×10^{-3} and 5×10^{-6} , respectively. The smaller discrimination of the transition states indicates either a substantial degree of bond breaking in the activation process or a higher permeability to electron transfer of Cl^- compared to F^- . In the case of F^- and OH^- the opposing trend is observed, the transition states displaying a higher discrimination than the ground states.



This comparison suggests either a substantial degree of bond making in the transition state or a higher electron permeability of OH^- vs. F^- . Finally, a comparison between N_3^- and F^- reveals a reversal in affinities in going from ground states to transition states. The constants for



are 10 and 0.04, respectively, and more efficient electron transfer by N_3^- than by F^- is indicated. The trends for the Fe^{2+} - FeX^{2+} exchange reactions are entirely analogous, and are presented, together with those for the Cr^{2+} - CrX^{2+} reactions, in Figure 2.

Orbital Symmetry Considerations

The relative electron-mediating ability of bridging ligands depends on the identity of the two metal centers involved in the redox reaction, and attempts have been made to correlate reactivity trends and electronic structure.^{54,70,71} The importance of the symmetry of donor and acceptor orbitals in determining the changes in bond lengths attending activation was noted,⁵⁴ as was the importance of matching the symmetry of metal and ligand orbitals in facilitating electron transfer.⁷⁰ The pertinent data are not very extensive, but some generalizations have been made.¹⁴ For electron transfer between e_g orbitals, $\text{Cl} > \text{N}_3^- \gg \text{CH}_3\text{CO}_2^-$. For transfer from an e_g to a t_{2g}

(70) J. Halpern and L. E. Orgel, *Disc. Faraday Soc.*, **29**, 32 (1960).
(71) H. Taube, *Proc. Robert A. Welch Conf. Chem. Res.*, **5** (1962).

orbital, $N_3^- > Cl^- \sim CH_3CO_2^-$. For transfer from a t_{2g} to an e_g orbital, $N_3^- \gg Cl^-$.

A possible explanation of the observed trends is based on orbital symmetry arguments.^{14,72} When the symmetries of the orbitals of the metal ions that donate and accept the electron are the same, bridging ligands with orbitals of matching symmetry may provide a lower energy pathway for electron transfer. Thus, if the reductant has the electron to be donated in an e_g -type orbital and the lowest acceptor orbital in the oxidant is also of e_g symmetry, then chloride, presumably being a σ carrier, is a "better" bridging ligand than azide or acetate. Conversely, when the electronic configurations of oxidant and reductant are such that the donor and/or acceptor orbital is of t_{2g} symmetry, the azide and acetate become effective bridging ligands, presumably because of favorable overlap of the t_{2g} orbital with the π system of azide or acetate.

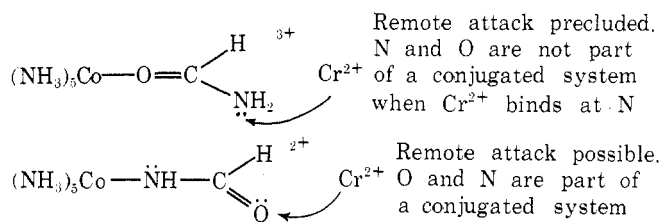
The faster rate of the pentaammineisonicotinamide-ruthenium(III)- Cr^{2+} reaction as compared to the corresponding cobalt(III) reaction has also been rationalized on the basis of symmetry considerations.⁷² In the former system, oxidant and bridging ligand have matching π symmetry (Ru(III) with a $t_{2g}^5 e_g^0$ electronic configuration accepts the incoming electron in a π -type orbital and the lowest unoccupied molecular orbital of the ligand has π symmetry), and once the electron is given up by the reductant to the bridging ligand, the overall electron transfer reaction is consummated. On the other hand, for the Co(III)- Cr^{2+} system, where oxidant and reductant have acceptor and donor orbitals of σ symmetry, but the carrier orbital has π symmetry, the resonance mechanism may become prohibitive, perhaps because of the difficulty in meeting simultaneously Franck-Condon and symmetry restrictions. Under these circumstances, a stepwise or chemical mechanism for electron transfer provides the lower energy pathway.

What Ligands Can Act as Bridges?

A basic, unshared pair of electrons in the bridging ligand is a necessary condition for the formation of a precursor binuclear complex and, therefore, for an inner-sphere electron transfer. This is, apparently, also a sufficient condition for reaction via adjacent attack, perhaps because direct exchange is possible between metal ions bridged by a single atom. For example, halides, OH^- , and SCN^- bound to an oxidant have a basic lone pair and act as bridging ligands. Bound water and oxygen-bonded urea have a lone pair in the lead-in atom, but the basicity of the oxygen is very low; CN^- and NCS^- (assuming that rehybridization does not take place) have no lone pair on C or N, respectively. Therefore, oxidants bound to the last four ligands do not feature inner sphere reductions *via* adjacent attack.

The availability of σ lone pair for binding the incoming metal ion is not a sufficient condition, however, for reaction via remote attack. Thus, in the Cr^{2+} reductions of the linkage isomers of formamidopentaamminecobalt(III),⁷³ the reaction of the O-bonded isomer proceeds by an outer-sphere mechanism,

whereas the reaction of the conjugate base of the N-bonded isomer features inner-sphere, remote attack.



The suggestion was made^{73,74} that necessary conditions for inner-sphere electron transfer *via* remote attack are a donor atom in the bridging ligand that has a lone pair of electrons available for σ bonding to the incoming metal, and that the two donor atoms of the bridging ligand must be part of a conjugated system extending between the two metal centers.

It must be noted that, although the conditions outlined above may be necessary to ensure remote attack, they are not sufficient. Thus, $Co(NH_3)_5O_2CC_6H_4-p-CO_2^+$ and $Co(NH_3)_5O_2CC_6H_4-p-CHO^{2+}$ feature a basic, remote oxygen in conjugation with the oxygen bound to the cobalt(III), but only in the reaction of the latter complex with Cr^{2+} is remote attack operative.⁶⁰ The difference in the two systems has been ascribed to the ease of reduction of the *p*-formylbenzoate ligand. Whether facile reduction of the bridging ligand is a prerequisite for electron transfer through extended conjugated systems has not been established, but it is noteworthy that all cases of bridged electron transfer through more than three atoms involve easily reduced ligands. However, since the comparisons are restricted to Co(III)- Cr^{2+} reactions, it may be that, because the symmetry of donor and acceptor orbitals (σ) does not match the symmetry of the carrier orbital (π), reaction can only take place via the chemical mechanism, and, consequently, an easily accessible lowest unoccupied molecular orbital of the ligand becomes necessary.

The Real Thing. Intramolecular Electron Transfer

It has been widely recognized that measurements of rates of intramolecular electron transfer within binuclear complexes could provide considerable insight into the details of the mechanism of electron transport between metal ions across ligands. Although a great deal of effort appears to have been expended in various laboratories to reach this goal, only in the last year has unequivocal evidence for intramolecular electron transfer been obtained. The difficulties can be traced to low equilibrium constants for the formation of precursor binuclear complexes from mononuclear reactants, to competitive outer-sphere pathways in systems where precursor complexes would have been expected to be sufficiently stable to produce deviations from mixed second-order kinetics,⁷⁵ or in general to the difficulty in finding appropriate pairs of metal ions with the appropriate coordination

(74) R. J. Balahura and R. B. Jordan, *J. Am. Chem. Soc.*, **93**, 625 (1971).

(75) The deviations from second-order kinetics observed in labile systems^{5,6,18} where there is appreciable association between the reactants have been interpreted on the basis of intramolecular electron transfer. However, the alternate mechanism whereby dissociation of the ion pair is followed by bimolecular electron transfer cannot be ruled out.

(72) H. Taube, *Ber. Bunsenges. Phys. Chem.*, **76**, 964 (1972).

(73) R. J. Balahura and R. B. Jordan, *J. Am. Chem. Soc.*, **92**, 1533 (1970).

Table III
Rate Constants for Intramolecular Electron Transfer
in $(\text{NH}_3)_5\text{Co}^{\text{III}}\text{LRu}^{\text{II}}(\text{NH}_3)_4\text{OH}_2^{4+}$

Complex	k , sec^{-1} ^a
$\text{Co}^{\text{III}}\text{O}_2\text{C}-\text{C}_5\text{H}_4\text{N}-\text{Ru}^{\text{II}}$	1×10^2 ^b
$\text{Co}^{\text{III}}\text{O}_2\text{CCH}_2-\text{C}_5\text{H}_4\text{N}-\text{Ru}^{\text{II}}$	1.6×10^{-2}
$\text{Co}^{\text{III}}\text{O}_2\text{C}-\text{C}_5\text{H}_3\text{N}-\text{Ru}^{\text{II}}$	1.6×10^{-3}
$\text{Co}^{\text{III}}\text{O}_2\text{CCH}_2-\text{C}_5\text{H}_3\text{N}-\text{Ru}^{\text{II}}$	5.5×10^{-3}

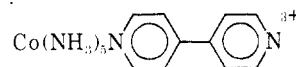
^a At 25°, 1 M toluenesulfonic acid. ^b In 0.1 M $\text{CF}_3\text{CO}_2\text{H}$; may have SO_4^{2-} instead of H_2O in the coordination sphere of $\text{Ru}(\text{II})$.

spheres and oxidation potentials to yield binuclear complexes that undergo internal electron transfer competitively with dissociation.

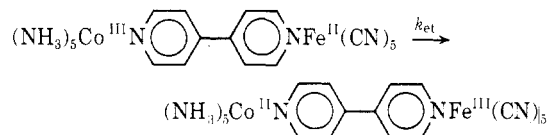
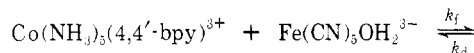
In order to circumvent these difficulties, a series of binuclear $\text{Ru}(\text{III})-\text{Co}(\text{III})$ complexes was synthesized and treated with a stoichiometric deficiency of a rapid one-electron reducing agent.⁷⁶ This produces a binuclear precursor complex in situ and, provided that electron transfer within the binuclear complex is slow compared to its rate of generation, the intramolecular electron transfer can be measured. This approach proved to be successful and to have a broad scope in the case of a series of $\text{Co}(\text{III})-\text{Ru}(\text{II})$ binuclear complexes bridged by pyridinecarboxylate ligands.⁷⁶ The results, summarized in Table III, show the importance of conjugation (decrease by a factor of 10^5 in going from 4-pyridinecarboxylate to 3-pyridinecarboxylate), the insulating effect of a CH_2 group (decrease by a factor of 10^4 in going from 4-pyridinecarboxylate to 4-pyridineacetate), and even the possibility of the actual electron-transfer path by-passing the bridging ligand and proceeding by an outer-sphere mechanism (3-pyridineacetate being somewhat faster than 3-pyridinecarboxylate, and subject

(76) S. S. Isied and H. Taube, *J. Am. Chem. Soc.*, **95**, 8198 (1973).

to rate acceleration with increasing $[\text{H}^+]$). Very recently, another successful approach to the measurement of intramolecular electron-transfer rates made use of the high affinity⁷⁷ of the $\text{Fe}(\text{CN})_5^{3-}$ moiety for nitrogen heterocycles and of the newly⁷⁸ devised synthesis of



The rate constants for the formation and dissociation of the binuclear precursor and for intramolecular electron transfer have been obtained.⁷⁹ This ap-



$$k_f = 5.5 \times 10^3 \text{ sec}^{-1}; k_d = 4.5 \times 10^{-3} \text{ sec}^{-1}; \\ k_{\text{et}} = 2.6 \times 10^{-3} \text{ sec}^{-1}$$

proach is being extended to other cobalt(III) complexes, and the importance of electronic and steric considerations is already apparent.⁸⁰ For the pentaaminepyridinecarboxylatocobalt(III) + $\text{Fe}(\text{C}-\text{N})_5\text{OH}_2^{3-}$ systems, with N in the 4 position, $k_{\text{et}} = 1.7 \times 10^{-4} \text{ sec}^{-1}$; with N in the 3 position, $k_{\text{et}} < 3 \times 10^{-5} \text{ sec}^{-1}$; and with N in the 2 position, the binuclear complex is not formed.

The author is grateful to the National Science Foundation for continuing support of his researches into the mechanism of electron-transfer reactions. The dedication, enthusiasm, and productivity of students and postdoctoral associates have made that continuing support possible.

(77) H. E. Toma and J. M. Malin, *Inorg. Chem.*, **12**, 1039 (1973); *ibid.*, **12**, 1080 (1973).

(78) A. Miralles, Ph.D. Thesis, State University of New York, Stony Brook, N.Y., July 1974.

(79) D. Gaswick and A. Haim, *J. Am. Chem. Soc.*, **96**, 7845 (1974).

(80) J. J. Jwo and A. Haim, work in progress.