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Nonbridging Ligand and Temperature Effects on the Rate of Reduction of Bromocobalt(III) Complexes by Iron(II)

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The rates of reduction by Fe^{2+} and the associated activation parameters for five amine complexes of Co(III) containing bromide as a ligand have been measured. The values of the second-order rate constants vary from 6.1×10^{-6} M^{-1} sec^{-1} (*cis*-$Co(en)_2NH_3Br^{2+}$) to 9.4×10^{-2} M^{-1} sec^{-1} (*trans*-$Co(en)_2H_2OBr^{2+}$) at 25° and $[ClO_4^-] = 1.0$ M. This variation in rate is caused by a variation in the enthalpy of activation (17.6 to 12.6 kcal mol^{-1}, respectively) with the entropy of activation nearly constant at -20 cal mol^{-1} deg^{-1}. The implications of these data on the mechanism of the reaction, the ability of Br^- to serve as a bridge, and the concept of nonbridging ligand effects are discussed.

Introduction

The effect of a change in nonbridging ligand on the rate of an electron-transfer process has been studied in several systems.[1,2] These data have allowed a systemization of the nonbridging ligand effects.[1-3] For oxidants in which an orbital of predominantly σ symmetry is to be populated[4] (complexes of Co(III) and Cr(III), for instance), the rates of reduction for a series of complexes with a given "bridging" ligand can usually be predicted, at least approximately, by rate measurement of a few of these complexes with the reductant of interest, followed by application of linear free energy relationships. This semiquantitative success in understanding the role of nonbridging ligands leads to the question of concern here. Can one learn something about the details of the role of the bridging ligand in inner-sphere oxidation–reduction reactions by application of nonbridging ligand studies?

Some attempts at utilizing nonbridging ligand effects as a "mild" perturbation have been made,[1,5,6] but these studies have been more concerned with mechanism than with attempts to understand rate patterns for reactions of a given mechanism. This report deals with a study of the reduction of some Co^{III}–Br^- complexes by Fe^{2+}: $Fe^{2+} + L_5Co^{III}Br = Fe^{3+} + Co^{2+} + Br^- + 5L$. The intent of the experiments was to establish if the bridging ligand, Br^-, depended on the nonbridging ligand perturbation in a fashion different from that of Cl^- as a bridging ligand. It was hoped that such information would be relevant to the question of why $Co(NH_3)_5Cl^{2+}$ is reduced more rapidly than $Co(NH_3)_5Br^{2+}$ by Fe^{2+},[7,8] although Cr^{2+},[9] V^{2+},[10] $Ru(NH_3)_6^{2+}$,[2,11] and other reducing agents react more rapidly with the latter.[12]

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(2) R. C. Patel and J. F. Endicott, *ibid.*, **90**, 6364 (1968), and references therein.
(3) R. G. Linck, *Inorg. Chem.*, **7**, 2394 (1968).
(4) W. G. Movius and R. G. Linck, *J. Amer. Chem. Soc.*, **92**, 2677 (1970).
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(6) K. W. Hicks and R. G. Linck, to be submitted for publication.
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(10) J. P. Candlin, J. Halpern, and D. L. Trimm, *J. Amer. Chem. Soc.*, **86**, 1019 (1964).
(11) J. F. Endicott and H. Taube, *ibid.*, **86**, 1686 (1964).
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In addition further information about nonbridging ligand phenomena has been obtained. The temperature dependencies of the reductions have been measured in order to attempt to understand how $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ individually affect nonbridging ligand reactivity. Another means of establishing mechanism by the nonbridging ligand perturbation has been investigated.

Experimental Section

Materials.—Solutions of ferrous perchlorate in perchloric acid were prepared and analyzed as previously described.[3] *trans*-$[Co(en)_2Br_2]Br$ was prepared from $[Co(en)_2CO_3]Br$.[13] *trans*-$[Co(en)_2Br_2]ClO_4$, *trans*-$[Co(en)_2OHBr]Br$,[14] and *cis*-$[Co(en)_2NH_3Br]Br_2$[15] were prepared from the *trans*-dibromo bromide salt according to the referenced procedures. $[Co(NH_3)_5Br]Br_2$ was prepared[16a] from $[Co(NH_3)_5CO_3]NO_3$.[16b] Purity of the indicated complexes was determined by spectroscopic methods and by analysis for cobalt. The latter analysis involved reduction of the complex with $SnCl_2 \cdot 2H_2O$ in HCl and evaporation to dryness, followed by solution of the solid in concentrated HCl. The extinction coefficient for Co(II) in concentrated HCl was found to be 561 ± 2 M^{-1} at 6910 Å. The results are presented in Table I.[14,17-20]

All other reagents were prepared as previously described[1] or by using reagent grade chemicals. Water was doubly distilled in a quartz apparatus.

Kinetic Measurements.—All kinetic studies were performed spectrophotometrically on a Cary Model 14 recording spectrophotometer. Solutions containing all reagents except one were thermostated in a spectrophotometer cell and the final one was then added. The order of addition depended on the complex; because of fairly rapid aquation[21] of *trans*-$Co(en)_2Br_2^+$ and isomerization[21] of *trans*-$Co(en)_2H_2OBr^{2+}$, these complexes were the last reagents to be added. The concentration of Fe^{2+} used was such that spontaneous aquation of the complexes was slight except in the case of *cis*-$Co(en)_2NH_3Br^{2+}$; in all cases where spontaneous aquation was >1% of the pseudo-first-order rate constant, the appropriate correction was applied (see Results). To generate *cis*-$Co(en)_2H_2OBr^{2+}$, an acidified solution of *trans*-$[Co(en)_2OHBr]Br$ was allowed to stand 7–10 half-lives[21]

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(14) S. C. Chan and M. L. Tobe, *J. Chem. Soc.*, 4531 (1962).
(15) M. L. Tobe and D. F. Martin, *Inorg. Syn.*, **8**, 198 (1966).
(16) (a) See ref 13, p 210; (b) F. Basolo and R. K. Murmann, *Inorg. Syn.*, **4**, 171 (1953).
(17) D. A. Buckingham, I. I. Olsen, and A. M. Sargeson, *J. Amer. Chem. Soc.*, **88**, 5443 (1966).
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(19) P. Benson and A. Haim, *J. Amer. Chem. Soc.*, **87**, 3826 (1965).
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TABLE I
ANALYSIS OF Co(III) COMPLEXES

Complex	ϵ,[a] M^{-1} cm^{-1}	λ,[a] Å	Ref	% Co Found	% Co Calcd
$[Co(NH_3)_5Br]Br_2$	54.5 (55.5, 54.2)	5490 (5500)	17, 18	15.75	15.36
trans-$[Co(en)_2Br_2]ClO_4$	49.6 (48.5)	6550 (6560)	19	13.82	13.44
trans-$[Co(en)_2OHBr]Br$	32.6 (33)[b]	6060 (6100)[b]	14	16.64	16.54
	13.8[b]	5200[b,c]			
cis-$[Co(en)_2NH_3Br]Br_2$	81.2 (81.5)	5395 (5390)	20	14.1	13.5

[a] Literature values are given in parentheses, wavelength of absorption maximum. [b] In acidic solution, 1.0 *M*. [c] Absorption minimum.

for isomerization to prepare the cis–trans equilibrium mixture. When Fe^{2+} was added to this mixture, the trans component was rapidly consumed, leaving pure *cis*-$Co(en)_2H_2OBr^{2+}$ and Fe^{2+}, which slowly reacted.

The reaction of Fe(II) with *cis*-$Co(en)_2NH_3Br^{2+}$ was too slow to examine continuously. Samples were sealed in vials and placed in a thermostated bath. From time to time the vials were removed from the bath and placed in a water-filled block in the compartment of the Cary. The absorbance was recorded and the sample was returned to the bath. The time necessary to take the point was insignificant compared to reaction time and hence temperature control during the time of measurement was not necessary.

All kinetic experiments were run under pseudo-first-order conditions with respect to $[Fe^{2+}]$. The wavelength of observation was such that the dominant absorbing species was the Co(III) complex. Usually this wavelength was on the edge of the charge-transfer transition. Plots of $\ln (A_t - A_\infty)$, where A_t is the absorbance at time t and A_∞ that at the end of the reaction, were linear. The pseudo-first-order rate constant was calculated from the slope.

Results

Kinetic Results.—The rates of the Fe^{2+} reduction of *trans*-$Co(en)_2Br_2^+$ [19] and $Co(NH_3)_5Br^{2+}$ [7,8] have been studied previously although the former at only one temperature and the latter at unit and 1.7 *M* ionic strengths rather than at $[ClO_4^-] = 1.0\ M$. The rate law proposed

$$\frac{-\,d[\mathrm{Co(III)}]}{dt} = k[\mathrm{Co(III)}][\mathrm{Fe(II)}]$$

is in accord with the data presented here. The Fe^{2+} reduction of *trans*-$Co(en)_2H_2OBr^{2+}$ also was found to follow this rate law. Data demonstrating this point and the independence of the rate on $[H^+]$ are shown in Table II. The second-order rate data for the three complexes have been corrected for isomerization or aquation using the literature values for these rate constants (*trans*-$Co(en)_2H_2OBr^{2+}$, isomerization rate 1.63×10^{-4} sec^{-1};[21] *trans*-$Co(en)_2Br_2^+$, aquation rate 1.39×10^{-4} sec^{-1};[21] $Co(NH_3)_5Br^{2+}$, aquation rate 6.3×10^{-6} sec^{-1} [22]). These corrections were always less than 6% of the observed pseudo-first-order rate constant. The values used to correct the data are probably not highly accurate due to variation in ionic strength,[23] but these differences are very small compared to the pseudo-first-order rate constants.

The value found for the rate of reduction of $Co(NH_3)_5Br^{2+}$ is in satisfactory agreement with the earlier studies.[7,8] This is true also for *trans*-$Co(en)_2Br_2^+$, although a higher precision was obtained with the data reported in Table II (see also below, Table V). Experiments were performed to test whether the solubility of *trans*-$[Co(en)_2Br_2]ClO_4$ might have been a factor in the scatter reported earlier.[19] To 37 ml of 1.00 *N* $HClO_4$ was added 0.03 g of *trans*-$[Co(en)_2Br_2]ClO_4$; this was stirred at 25° for 5 min and then filtered and the spectrum was recorded. The concentration in solution determined with ϵ 49.6 M^{-1} cm^{-1} (Table I) was $5.1 \times 10^{-4}\ M$. To test whether equilibrium had been achieved, the measurement was repeated by mixing 0.03 g of *trans*-$[Co(en)_2Br_2]ClO_4$, dissolved in 10 ml of water, with 10 ml of 2.00 *N* $HClO_4$, both thermostated at 25°. After stirring for 1 min and filtering, the spectral analysis was made. The concentration of *trans*-$Co(en)_2Br_2^+$ was found to be $9.2 \times 10^{-4}\ M$.[24] The solubility of *trans*-$[Co(en)_2Br_2]ClO_4$ is thus greater than $5 \times 10^{-4}\ M$ but less than $9 \times 10^{-4}\ M$. It is concluded

TABLE II
Fe^{2+} REDUCTION OF SEVERAL Co^{III}–Br COMPLEXES AT 25° AND $[ClO_4^-] = 1.0\ M$

$10^4[\mathrm{Co(III)}]_0$, *M*	$10[Fe^{2+}]$, *M*	$[H^+]$, *M*	*k*,[a] M^{-1} sec^{-1}
	A. *trans*-$Co(en)_2H_2OBr^{2+}$ [b]		
1.9	0.263	0.95	9.03×10^{-2}
1.9	0.524	0.30[c]	9.39×10^{-2}
2.0	0.409	0.92	9.36×10^{-2}
6.0	0.595	0.77	9.35×10^{-2}
7.5	0.583	0.89	9.92×10^{-2}
		Av	$(9.41 \pm 0.32) \times 10^{-2}$
	B. *trans*-$Co(en)_2Br_2^+$ [d]		
1.0	1.14	0.77	1.80×10^{-2} [e]
1.3	1.78	0.64[f]	2.03×10^{-2} [e]
1.9	3.56	0.28	1.88×10^{-2} [g]
2.3	2.67	0.32	1.85×10^{-2} [g]
2.7	3.39	0.26	1.82×10^{-2} [g]
		Av[h]	$(1.85 \pm 0.03) \times 10^{-2}$
	C. $Co(NH_3)_5Br^{2+}$ [b]		
6.2	1.55	0.69	8.26×10^{-4}
8.6	2.15	0.57	8.75×10^{-4}
9.9	2.47	0.51	9.49×10^{-4}
12.0	2.99	0.40	8.58×10^{-4}
13.0	3.22	0.35	9.36×10^{-4}
		Av	$(8.89 \pm 0.52) \times 10^{-4}$

[a] Corrected for aquation or isomerization; the standard deviation is given. [b] Wavelength of observation 3350 Å. [c] $[Li^+] = 0.60\ M$. [d] Wavelength of observation 3300 Å. [e] 24.3°. [f] $[Br^-] = 0.61\ M$. [g] 24.7°. [h] Average of values at 24.7°.

(22) J. N. Brønsted and R. Livingston, *J. Amer. Chem. Soc.*, **49**, 435 (1927).

(23) R. G. Linck, *Inorg. Chem.*, **7**, 1018 (1968).

(24) More careful approach to equilibrium is precluded by the relatively rapid aquation of *trans*-$Co(en)_2Br_2^+$. It takes only about 2 min for 2% of the complex in solution to aquate.

that the greater precision of the data obtained here is due to the lower concentration of complex used; it seems likely that collapse of supersaturated solution or reaction at solid–liquid interfaces would cause scatter in kinetic experiments.

The rate laws for the reduction of both *cis*-$Co(en)_2NH_3Br^{2+}$ and *cis*-$Co(en)_2H_2OBr^{2+}$ are complicated by other factors. In the case of *cis*-$Co(en)_2NH_3Br^{2+}$, the rate of reduction by Fe(II) at concentrations of Fe(II) that are less than 0.5 *M* is comparable to the rate of aquation. Thus the rate law for the disappearance of *cis*-$Co(en)_2NH_3Br^{2+}$ is

$$\frac{-\,\mathrm{d}[cis\text{-}Co(en)_2NH_3Br^{2+}]}{\mathrm{d}t} = \{k_a + k[Fe(II)]\}[Co(III)]$$

At a fixed [Fe(II)], the observed pseudo-first-order rate constant, k_{obsd}, is composed of two terms. Plots of k_{obsd} *vs.* [Fe(II)] yielded values k_a and k. Table III

TABLE III

THE RATE OF DISAPPEARANCE OF *cis*-$Co(en)_2NH_3Br^{2+}$ AT 25° AND $[ClO_4^-]$ = 1.0 *M*

10^3 [Co(III)]$_0$, *M*	10[Fe(II)]$_0$, *M*	[H$^+$], *M*	10^6k_{obsd},[a] sec^{-1}	10^6k_{calcd},[b] sec^{-1}
6.51	0	1.00	1.22	1.04
1.30	0	1.00	0.96	1.04
5.21	0.92	0.81	1.45	1.60
2.60	2.77	0.45	2.87	2.73
1.30	3.69	0.26	3.26	3.29

[a] Wavelengths of observation 3500 and 5400 Å. [b] Calculated from the parameters indicated in the text and the equation $k_{calcd} = k_a + k[Fe(II)]$.

illustrates this data at 25°. The values in the last column were calculated from the least-squares parameters $k_a = (1.04 \pm 0.10) \times 10^{-6}$ sec^{-1} and $k = (6.12 \pm 0.5) \times 10^{-6}$ M^{-1} sec^{-1}. The agreement is considered adequate. In addition the value of k_a agrees with that extrapolated from the data of Nyholm and Tobe at higher temperatures, 1.09×10^{-6} sec^{-1}.[20] Spectral examination of solutions at equilibrium indicated that *cis*-$Co(en)_2NH_3H_2O^{2+}$ was the Co(III) species remaining.[20] Fe(II) reacts with this species extremely slowly.

The rate of reduction of *cis*-$Co(en)_2H_2OBr^{2+}$, like that of *cis*-$Co(en)_2H_2OCl^{2+}$ [19] and *cis*-$Co(NH_3)_4H_2OCl^{2+}$,[3] also follows a two-term rate law

$$\frac{-\,\mathrm{d}[Co(III)]}{\mathrm{d}t} = \{k_i + k[Fe(II)]\}[Co(III)]$$

As before, the first term is interpreted as being due to an isomerization; that of *cis*-$Co(en)_2H_2OBr^{2+}$ to the trans isomer, followed by rapid reduction of the trans isomer. The second term represents direct reduction of the *cis* complex. Table IV illustrates some data and the fit of those data to the parameters $k_i = (5.28 \pm 0.31) \times 10^{-5}$ sec^{-1} and $k = (2.80 \pm 0.15) \times 10^{-4}$ M^{-1} sec^{-1}. The former parameter is in reasonable agreement with direct measurement of the isomerization rate in 0.01 *N* HNO_3,[21] although this agreement appears somewhat fortuitous (see below).

Temperature Dependence.—All of the reactions discussed above were repeated at a series of temperatures in order to obtain the activation parameters for the reactions. These results are tabulated for the various reactions in Table V. In all cases the activation parameters are those calculated by nonlinear minimization of the sum of the squares of the deviations between observed and calculated rate constants.[25] (The points were weighed according to k_{obsd}^{-2}.) In the case of *cis*-$Co(en)_2NH_3Br^{2+}$ and *cis*-$Co(en)_2H_2OBr^{2+}$, the simultaneous fit of the observed pseudo-first-order rate constants at all temperatures and concentrations of Fe(II) was employed. The precision indices are the standard deviations of the parameters. Comparison of the data for $Co(NH_3)_5Br^{2+}$ in Table V with those previously reported by Diebler and Taube[8] ($\Delta H^{\ddagger} = 14.5 \pm 0.6$ kcal mol^{-1} and $\Delta S^{\ddagger} = -23 \pm 2$ cal mol^{-1} deg^{-1}, ionic strength 1.7 *M*) and Espenson[7] ($\Delta H^{\ddagger} = 12.5 \pm 1.2$ kcal mol^{-1} and $\Delta S^{\ddagger} = -30 \pm 5$ cal mol^{-1} deg^{-1}, ionic strength 1.0 *M*, six experiments over a 10° temperature range) indicates satisfactory, although not excellent, agreement. The value found for $\Delta H^{\ddagger}$ of the reaction *cis*-$Co(en)_2H_2OBr^{2+} \rightarrow$ *trans*-$Co(en)_2H_2OBr^{2+}$ is somewhat higher than that calculated from the data of Chan and Tobe,[21] $\Delta H^{\ddagger} = 27$ kcal mol^{-1}, although this discrepancy may be due to ionic strength differences.

TABLE IV

THE RATE OF REDUCTION OF *cis*-$Co(en)_2H_2OBr^{2+}$ BY Fe(II) AT 25° AND $[ClO_4^-]$ = 1.0 *M*

10^3 [Co(III)]$_0$,[a] *M*	10 [Fe(II)]$_0$, *M*	[H$^+$], *M*	10^4k_{obsd},[b] sec^{-1}	10^4k_{calcd},[c] sec^{-1}
7.9	1.13	0.77	0.86	0.84
6.6	1.70	0.65	1.01	1.00
5.3	2.26	0.54	1.15	1.16
4.0	2.83	0.43	1.33	1.32
5.0	1.70	0.52[d]	0.98	1.00

[a] [Co(III)] in total, including some trans isomer; see text. [b] Wavelength of observation 3500 Å. [c] Calculated from the parameters quoted in the text by the equation $k_{calcd} = k_i + k[Fe(II)]$. [d] [Li$^+$] = 0.13 *M*.

Discussion

It has previously been shown that the Fe^{2+} reductions of several Co^{III}–Cl^- systems are inner sphere.[26] Similar experiments with the Fe^{2+} + Co^{III}–Br^- systems are not possible because of the great lability[27] of $FeBr^{2+}$ compared to $FeCl^{2+}$.[28] The similarity in the reactivity patterns of the Co^{III}–Br^- systems and the Co^{III}–Cl^- systems, however, supports the assumption of a similar mechanism. The mechanism of the reaction of Fe^{2+} with Co^{III}–Br^- complexes will be assumed in the discussion that follows to be inner sphere; comments on the factors that prejudice this choice of mechanism will be presented.

Nonbridging Ligand Effects.—The rates of reduction

(25) The computer program uses the method of Gauss to linearlize the equations; it closely follows the procedure described by R. H. Moore and R. K. Ziegler, Report LA 2367, Los Alamos Scientific Laboratory, Los Alamos, N. M., 1960.

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

(27) P. Matthies and H. Wendt, *Z. Phys. Chem. (Frankfurt am Main)*, **30**, 137 (1961).

(28) E. G. Moorhead and N. Sutin, *Inorg. Chem.*, **6**, 428 (1967), and references therein.

TABLE V

RESULTS ON THE RATES OF REDUCTION AS A FUNCTION OF TEMPERATURE[a] AT $[ClO_4^-] = 1.0\ M$

	$10[Fe(II)]$, M	$[H^+]$, M	n[b]	Temp, °C	k, $M^{-1}\ sec^{-1}$	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, cal $mol^{-1}\ deg^{-1}$
trans-$Co(en)_2Br_2^+$	1.64–3.66	0.26–0.66	4	33.2	$(3.91 \pm 0.08) \times 10^{-2}$	14.8 ± 0.2	-16.7 ± 0.6
	1.53–2.91	0.41–0.69	4	16.0	$(8.68 \pm 0.20) \times 10^{-3}$		
trans-$Co(en)_2H_2OBr^{2+}$	0.19–1.42	0.71–0.96	4	33.2	$(1.67 \pm 0.10) \times 10^{-1}$	12.6 ± 0.3	-20.8 ± 1.1
	0.37–0.96	0.81–0.92	3	16.0	$(4.57 \pm 0.15) \times 10^{-2}$		
$Co(NH_3)_5Br^{2+}$	1.32–2.15	0.57–0.74	5	30.9	$(1.47 \pm 0.02) \times 10^{-3}$	15.5 ± 0.3	-20.4 ± 1.0
	1.37–2.89	0.42–0.73	5	17.8	$(4.41 \pm 0.08) \times 10^{-4}$		
cis-$Co(en)_2H_2OBr^{2+}$	0.92–2.82	0.43–0.81	5	32.7	*c*	15.4 ± 0.8[d]	-23.2 ± 2.7[d]
	1.39–2.61	0.47–0.72	5	17.0			
cis-$Co(en)_2NH_3Br^{2+}$	0.66–1.55	0.69–0.87	3	40.4			
	0–1.97	0.61–1.00	5	43.1	*c*	17.6 ± 1.5[e]	-23.2 ± 5.0[e]
	0–1.97	0.61–1.00	5	48.6			

[a] Data at 25° are presented in Tables II–IV. [b] Number of experiments in the indicated ranges. [c] The rate law is a function of $[Fe^{2+}]$; see text. [d] The activation parameters for the isomerization of *cis*-$Co(en)_2H_2OBr^{2+}$ to the trans species are $\Delta H^{\ddagger} = 31.4 \pm 0.8$ kcal mol^{-1} and $\Delta S^{\ddagger} = 27.5 \pm 2.6$ cal $mol^{-1}\ deg^{-1}$. [e] The activation parameters for the aquation of $Co(en)_2NH_3Br^{2+}$ are $\Delta H^{\ddagger} = 23.7 \pm 0.6$ kcal mol^{-1} and $\Delta S^{\ddagger} = -6.5 \pm 2.0$ cal $mol^{-1}\ deg^{-1}$.

of these Co^{III}–Br^- complexes follow the same ordering as the rates of reduction of Co^{III}–Cl^- complexes by Fe^{2+},[19] $Ru(NH_3)_6^{2+}$,[2] and V^{2+}.[1] The rate of reduction of a complex with an H_2O trans to the bridging group is very rapid compared to a complex with an ammonia trans to the bridging group. More quantitatively, the sensitivity to a change in nonbridging ligands may be obtained by plotting log $k_{Co^{III}Br}$ *vs.* log $k_{Co^{III}Cl}$ as is done in Figure 1. The slope of the line in this plot is

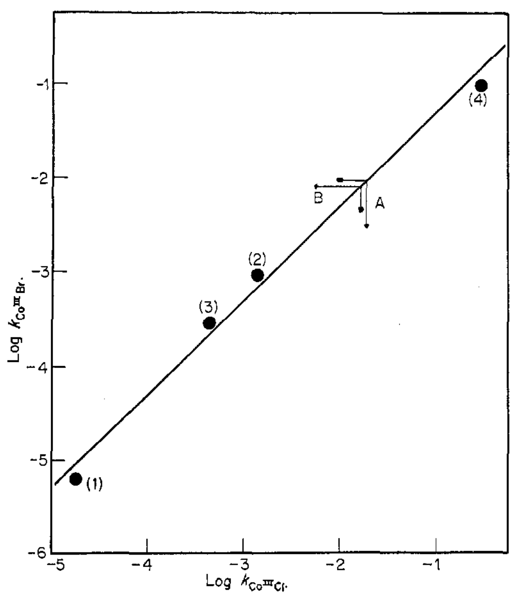

Figure 1.—Log $k_{Co^{III}Cl}$ *vs.* log $k_{Co^{III}Br}$ for the reaction of analogous Co(III) complexes containing chloride and bromide with Fe^{2+}: (1) *cis*-$Co(en)_2NH_3X^{2+}$; (2) $Co(NH_3)_5X^{2+}$; (3) *cis*-$Co(en)_2H_2OX^{2+}$; (4) *trans*-$Co(en)_2H_2OX^{2+}$. The arrow marked A indicates the predicted rate consant for a chloro-bridged *trans*-$Co(en)_2BrCl^+$ reduction; that marked B indicates the predicted rate constant for the same complex, but bromo bridged.

1.00 ± 0.08. That is, a change in nonbridging ligands has the same effect on the reaction of a Co^{III}–Br^- complex with Fe^{2+} as it does on the reaction with a Co^{III}–Cl^- complex. This is true over a reactivity range of greater than 10^4.

What is implied by this identical sensitivity is that the transition states $[L_5CoClFe^{n+}]^{\ddagger}$ and $[L_5CoBrFe^{n+}]^{\ddagger}$ do not put different demands on the nonbridging ligands. Presumably in both cases the nature of the nonbridging ligands and their σ-bonding ability determine in a gross fashion the energy necessary to reach the intersection of the energy surfaces of reactants and products (zero-order surface in the nomenclature of Reynolds and Lumry[29]). On the other hand, the interaction of the zero-order states, an effect which splits the two states to yield the nonintersecting energy surfaces, along the lower of which the reaction proceeds, would appear not to depend differently on the nature of the nonbridging ligand as the bridging ligand changes from Br^- to Cl^-. The simplest conclusion consistent with this analysis and the data is that the effects of nonbridging ligands and the bridging ligand are separable in determining $\Delta F^{\ddagger}$: a change in nonbridging ligands makes an equal change in $\Delta F^{\ddagger}$ for the $Fe^{2+} + Co^{III}$–Cl^- system as it does for the $Fe^{2+} + Co^{III}$–Br^- system; a change in the bridging ligand from Cl^- to Br^- makes the same change in $\Delta F^{\ddagger}$ regardless of the remaining ligands in the coordination sphere of Co(III). (This conclusion implicitly implies that nonbridging ligand variations do not affect the energy to form the precursor complex.) The analysis presented can be used as evidence that the reactivity pattern observed for Fe^{2+} reacting with Co(III) complexes, $F^- > Cl^- > Br^-$, is due to the nature of this reducing center: perturbation of the energy of the transition state by a change localized on the oxidant center cannot affect the order of reactivity. Hence no peculiar feature of oxidant *and* reductant is responsible for the reactivity order. This conclusion is not new; it has previously been proposed by Sutin[12] and by Carlyle and Espenson.[30] The evidence presented here supports this conclusion on the basis of systems in which the perturbation is milder.

The experiments described above serve to establish how the enthalpy and entropy of activation vary as the nonbridging ligands are changed. As can be seen from Table V the change in reactivity of all the complexes

(29) W. L. Reynolds and R. W. Lumry, "Mechanisms of Electron Transfer," The Ronald Press, New York, N. Y., 1966, p 74 ff.

(30) D. W. Carlyle and J. H. Espenson, *J. Amer. Chem. Soc.*, **91**, 599 (1969); see also N. Sutin, *Accounts Chem. Res.*, **1**, 225 (1968).

between *trans*-$Co(en)_2H_2OBr^{2+}$, $k = 9.4 \times 10^{-2}\ M^{-1}\ sec^{-1}$ at 25°, and *cis*-$Co(en)_2NH_3Br^{2+}$, $k = 6.1 \times 10^{-6}\ M^{-1}\ sec^{-1}$, is caused primarily by the change in $\Delta H^{\ddagger}$. Indeed, if one compares only the oxidants with a dipositive charge $\Delta S^{\ddagger}$ ranges only from −20.4 to −23.2 cal mol^{-1} deg^{-1}. $\Delta S^{\ddagger}$ for *trans*-$Co(en)_2Br_2^+$, the only monopositive ion studied, is only −16.7 cal mol^{-1} deg^{-1}. These results mean that over a range of temperature, the efficiency of the nonbridging ligand will be maintained in substantially the same order as found at 25°. The perturbation caused by a change in the nonbridging ligands is primarily electronic in nature. The effect can be visualized as proportional to the energy measured by the charge-transfer transition (a process governed by the Franck–Condon principle)

$$\underset{\text{I}}{Fe^{II}(H_2O)_5BrCo^{III}L_5} \longrightarrow \underset{\text{II}}{Fe^{III}(H_2O)_5BrCo^{II}L_5}$$

The perturbation of the Co(III) center by the nonbridging ligand changes the energy of the acceptor orbital and changes the charge-transfer energy, which in turn affects the point of intersection of the two zero-order states represented by I and II. Such an effect should manifest itself through the enthalpy of activation as is observed in the data presented here. This analysis is based upon that presented more quantitatively by Hush.[31]

Mechanistic Conclusions with Nonbridging Ligand Effects.—The close correspondence in the rate of reduction of the complexes with Br^- as the possible bridge as compared to the rate of reduction of those with Cl^- as the possible bridge strongly implies a similar mechanism for both systems. If the mechanisms differed, one would expect at least a slope in Figure 1 different from 1.0.[1] In addition, the strong implication to be drawn from the temperature dependence data is that all the Co^{III}–Br^- complexes react by the same mechanism.

Figure 1 also illustrates what may become a relatively useful means of distinguishing between two possible bridges in a given complex. The case in point is the geometry of the activated complex for the Fe^{2+} reduction of *trans*-$Co(en)_2BrCl^+$. The rates of reduction of *trans*-$Co(en)_2Br_2^+$ and *trans*-$Co(en)_2Cl_2^+$, corrected for the statistical factor of 2, give measures of the respective nonbridging abilities of Br^- and Cl^-. The arrow marked A in Figure 1 indicates how the rate of a Br^- nonbridging ligand with a Br^- bridge predicts the rate for a Cl^- bridge and Br^- nonbridging ligand. Similarly the arrow marked B indicates the predicted ability of Cl^- to function as a nonbridging ligand when Br^- is the bridge. These considerations indicate that Br^- is a more efficient nonbridging ligand than is Cl^- (a conclusion consistent with the σ-bonding model of nonbridging ligand effects in which similar molecules and ions are compared by consideration of their pK's[32]). Thus both the bridging efficiency, $Cl^- > Br^-$, and the nonbridging efficiency, $Br^- > Cl^-$, are such as to make the transition state geometry $[BrCoL_4ClFe^{3+}]^{\ddagger}$ more stable than the Br^- bridged transition state $[ClCoL_4BrFe^{3+}]^{\ddagger}$. Nevertheless, the difference in stability of these two transition states is, as Benson and Haim originally suggested might be possible,[19] small. Further work on other systems is needed to establish this point in a more quantitative fashion.

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Infrared and Nuclear Magnetic Resonance Spectra of Thiocyanatotrimethylplatinum(IV) and Its Pyridine Adducts

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Infrared and nmr methods are used to deduce the structure of tetrameric thiocyanatotrimethylplatinum(IV). This unusual structure contains SCN bridging ligands with the sulfur bound to two platinum atoms and the nitrogen to one platinum atom. The 1:1 and 2:1 pyridine adducts (per platinum atom) were prepared and studied to assist in making assignments.

In extending our studies of tetrameric trimethylplatinum derivatives[2] we have considered bridging ligands containing sulfur, including thiocyanate. The ability of platinum compounds to exhibit several bonding modes with thiocyanate ions has been reported.[3] The occurrence of terminal sulfur- and nitrogen-bonded ligands as well as bridging SCN ligands has been reported.[4–6]

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