Table I. Shift and Line Broadening Data for $Mn^{II}PhDTA^a$

Temp, °C	Shift, Hz	Q, K	Δ, Hz	$10^5 T_{2'p}$, s
26.3	151 ± 36	4.42	2869 ± 37	0.55
39.2	138 ± 21	4.22	2118 ± 30	0.71
49.2	131 ± 2	4.13	1096 ± 8	1.43
59.2	125 ± 2	4.07	736 ± 24	2.13
69.0	122 ± 2	4.09	495 ± 7	3.17
83.8	118 ± 5	4.12	341 ± 29	4.60

[a] Here Q is defined as $TS[H_2O]/[Mn]$ and $T_{2'p}$ as $[Mn]/\pi\Delta$ and T is the Kelvin temperature, S is the relative shift ($\Delta\nu/\nu_0$), and Δ the line broadening in Hz. The errors are average deviations of five or six separate measurements at each temperature. The frequency was 11.495 MHz.

even a possible increase in coordination. The A/h per H_2O of $Mn(H_2O)_6^{2+}$ is, for example, $(5.8 \pm 0.2) \times 10^6$ Hz from our latest measurements. Seven-coordination is not unreasonable and thus the constancy of A/h seems to hold in this case, as well as in systems we have so far studied. A theoretical explanation for this observation is lacking. We can only suggest that the "S" state ion is largely ionically bound to the ligands.

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Registry No. $Mn^{II}(PhDTA)(H_2O)^{2-}$, 63658-44-6; $Co^{II}(PhDTA)^{2-}$, 63625-64-9.

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Kinetics of Substitution in $Cr(en)_2LBr^{n+}$ Complexes

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The mechanism of substitution on Cr(III) centers of the type $Cr(NH_3)_5X^{2+}$ or $Cr(H_2O)_5X^{2+}$ has recently been reviewed by Swaddle;[1] he has concluded on the basis of free energy correlations[2] and studies of the volume of activation[3] that the mechanism of such substitution is associative, I_a in the nomenclature of Langford and Gray.[4] This conclusion is to be contrasted with that of $Co(NH_3)_5X^{2+}$ complexes in which an I_d mechanism has been assigned.[4-6] We were interested in examining the consequences of this difference in the series of molecules of stoichiometry $M(en)_2ABr^{n+}$, in which Br^- is aquated, A is the "directing" group, and M is Co(III) or Cr(III). The data for the Co(III) complexes have long been available; the work that we report here allows the desired examination to be made.

Experimental Section

Materials. ***cis*-$[Cr(en)_2H_2OBr]Br_2 \cdot H_2O$.** Four and one-half grams of *cis*-$[Cr(en)_2Cl_2]ClO_4$[7] was dissolved in 40 mL of water and heated until the complex was in solution; the solution was cooled and a few drops of acetic acid added, followed by 7.5 g of $NaNO_2$ and 11.5 g of $NaClO_4$. The precipitate, which formed slowly, was removed, washed with ethanol, and dried; yield 2.9 g of *cis*-$[Cr(en)_2(ONO)_2]ClO_4$.[8] This material was treated with 15 mL of 2.0 N HBr, warmed to 60 °C, and then treated with 15 mL of concentrated HBr, heated for 5 min, and cooled. The precipitate was removed by filtration, washed with ethanol, and dried; yield 1.3 g (36%). Recrystallization was achieved by dissolving the material in 7 mL of 2.0 N $HClO_4$, filtering, and adding 5 mL of concentrated HBr to precipitate the product. Anal. Calcd for *cis*-$[Cr(en)_2H_2OBr]Br_2 \cdot H_2O$: Cr, 11.61. Found: Cr, 11.67. The spectroscopic parameters are λ_{max}, Å (ϵ, M^{-1} cm^{-1}): 5160 (72.9) and 3870 (59.4); lit.[9] values 5190 (72.2) and 3870 (60.5).

trans-$[Cr(en)_2H_2OBr]Br_2$ was prepared from *trans*-$[Cr(en)_2F_2]ClO_4$ as described by Fee, Harrowfield, and Jackson.[10] Anal. Calcd for *trans*-$[Cr(en)_2H_2OBr]Br_2$: Cr, 12.09. Found: Cr, 11.91. The spectroscopic parameters are λ_{max}, Å (ϵ, M^{-1} cm^{-1}): 5610 (22.4), 4550 (22.5), and 3830 (44.9); lit. values[9] 5610 (23.2), 4550 (24.9), and 3840 (44.8).

The 2-amino-2-(hydroxymethyl)-1,3-propanediol was from Eastman Kodak and was recrystallized from water prior to use. Pyridine was obtained from J. T. Baker. A solution of acidic ($HClO_4$) $LiClO_4$ was prepared from $LiCO_3$ and G. F. Smith perchloric acid with doubly distilled water.

Techniques. Kinetic runs were accomplished as follows: after separate thermostating of a dilute acidic solution of the Cr(III) complex and the base, 2-amino-2-(hydroxymethyl)-1,3-propanediol (whose concentration was chosen sufficiently high to act as a buffer), these two solutions were mixed, causing rapid deprotonation, followed by slower loss of Br^-. This latter step was monitored in the thermostated compartment of a Cary Model 14 recording spectrophotometer. The pH of the solutions was measured on a Radiometer Model 51 meter. Data points from kinetic runs were analyzed by a nonlinear least-squares computer program.

Results

Kinetics of *trans*-$Cr(en)_2OHBr^+$ Aquation. The rate of aquation of Br^- from *trans*-$Cr(en)_2OHBr^+$ was measured by the change in absorbance at 5800 Å. To confirm that this absorbance represents the desired reaction

$$trans\text{-}Cr(en)_2OHBr^+ \xrightarrow{k_b} Cr(en)_2(OH)(H_2O)^{2+} + Br^- \qquad (1)$$

we quenched a reacting solution after 5 half-lives by adding excess acid and examined the products spectrophotometrically. Using the spectral data of Woldbye,[11] we established that the resulting spectrum was that expected for *trans*-$Cr(en)_2(H_2O)_2^{3+}$ with small amounts of *trans*-$Cr(en)_2H_2OBr^{2+}$ and *cis*-$Cr(en)_2(H_2O)_2^{3+}$. A quenching experiment at 10 half-lives confirmed that the source of the *cis*-$Cr(en)_2(H_2O)_2^{3+}$ was from the primary reaction and was not a result of isomerization of the products. The stoichiometry of the reaction is thus as indicated in eq 1 with the composition of the product species being 95% trans and 5% cis. (Of course, the state of protonation of the product depends on the pH of the solution.) Further confirmation of the stoichiometric assignment is achieved by comparison of the value of the absorbance observed after 10 half-lives, A_{00}, with that calculated on the basis of the extinction coefficients and K_a of the product species. For our experiment at pH 8.1, where the dominant product is *trans*-$Cr(en)_2(OH)_2^+$, we find $A_{00} = 0.485$ and calculate $A_{00} = 0.515$. At pH 7.13, where more *trans*-$Cr(en)_2OHH_2O^{2+}$ is present, we find $A_{00} = 0.535$ and calculate $A_{00} = 0.531$. The calculated and observed values agree within the errors generated by reading extinction coefficients off of Woldbye's graphs.[11]

The rate of loss of Br^- was studied at three temperatures over a range of [Cr(III)] from 7.4 to 13.0×10^{-3} M. There is no dependence on $[H^+]$ over the range pH 6.15–8.20, as can be seen from the data in Table I. Also to be found there are the calculated rate constants determined by nonlinear least-squares treatment of the k,T points.

To verify that the process was understood and to determine a kinetic value for the acidity of *trans*-$Cr(en)_2H_2OBr^{2+}$, we

Table I. Rate of Aquation of *trans*-$Cr(en)_2OHBr^+$ (I = 1.0 M $LiClO_4$)

pH	T, °C	10^2k(obsd), s^{-1}	10^2k(calcd),[a] s^{-1}
7.15	11.1	1.16	1.18
7.25	11.1	1.02	
6.75	11.3	1.31	1.20
6.30	11.3	1.30	
6.37	11.3	1.40	
6.86	11.3	1.30	
6.15	11.3	1.20	
8.10	11.3	1.17	
7.13	11.4	1.14	1.22
6.83	11.5	1.14	1.23
6.85	11.5	1.32	
6.81	11.5	1.26	
7.6	11.5	1.17	
6.71	11.5	1.21	
6.65	11.5	1.23	
7.59	25.0	5.71	5.45
6.85	25.0	5.77	
6.90	25.0	5.65	
6.85	25.0	5.66	
8.1	33.2	12.0	12.6
7.6	33.2	12.2	
8.2	33.2	12.5	
8.41	33.2	12.3	

[a] The parameters are $\Delta H^\ddagger$ = 18.0 ± 0.3 kcal mol^{-1} and $\Delta S^\ddagger$ = −4.0 ± 0.9 cal mol^{-1} deg^{-1}.

Table II. Rate of Aquation of *cis*-$Cr(en)_2OHBr^+$ (I = 1.0 M $LiClO_4$)

pH	T, °C	10^2k(obsd), s^{-1}	10^2k(calcd),[a] s^{-1}
8.58	10.2	0.84	0.87
8.90	10.2	0.83	
8.15	10.2	0.90	
7.74	10.2	0.89	
8.00	10.2	0.83	
7.90	10.2	0.87	
7.52	10.2	0.83	
8.08	25.0	4.8	4.8
8.10	25.0	5.1	
7.38	25.0	4.7	
8.16	25.0	4.8	
7.63	25.0	5.0	
8.44	25.0	4.5	
8.04	25.0	4.9	
8.06	32.5	11.0	11.0
7.94	32.5	10.9	
8.38	32.5	10.7	
7.98	32.5	11.1	

[a] The parameters are $\Delta H^\ddagger$ = 19.5 ± 0.2 kcal mol^{-1} and $\Delta S^\ddagger$ = 0.8 ± 0.5 cal mol^{-1} deg^{-1}.

performed two experiments in acidic solution. Under these conditions, the mechanism

$$trans\text{-}Cr(en)_2H_2OBr^{2+} \xrightarrow{k_a} Cr(en)_2(H_2O)_2{}^{3+} + Br^-$$
$$trans\text{-}Cr(en)_2H_2OBr^{2+} \overset{K}{=} trans\text{-}Cr(en)_2OHBr^+ + H^+ \qquad (2)$$

and eq 1 lead to the observed rate constant

$$k_{obsd} = (k_a[H^+] + k_bK)/(K + [H^+])$$

In the range of values of $[H^+]$ we used, 3.1 → 6.3 × 10^{-4} M,[12] the value of k_a given by Quinn and Garner[9] is negligible. We find from our k_{obsd} values and a known k_b (Table I) that K = 6.8 × 10^{-6} and 7.0 × 10^{-6} M, respectively, in the two experiments.

Kinetics of *cis*-$Cr(en)_2OHBr^+$ Aquation. This reaction was measured by the absorbance change at 5900 Å. The stoichiometry was determined by quenching experiments as described above for the trans isomer. Within experimental error, the reaction stoichiometry is

$$cis\text{-}Cr(en)_2OHBr^+ \rightarrow cis\text{-}Cr(en)_2OHH_2O^{2+} + Br^- \qquad (3)$$

where the state of protonation of the product complex depends on pH. The kinetics of the reaction, which was examined over a series of pH values, indicated the absence of $[H^+]$ dependency in the rate law in the range of pH 7.38–8.90. (Note that in this range of $[H^+]$ there is no indication of a base-catalyzed term in the rate law such as that reported[13] in the aquation of *cis*-$Cr(en)_2OHCl^+$ in the pH range 10.12–10.70.) The data at three temperatures along with the calculated rate constants based on the nonlinear least-squares k–T dependency are given in Table II.

Discussion

The rate of aquation of a common ligand, X^-, from a series of complexes $Co(en)_2LX^{n+}$, where L varies, may be interpreted by consideration of the extra stability that L gives to a dissociative transition state relative to the ground state. Empirically the order of lability for some π-donor ligands is NH_2^- > OH > Br^- > NCS^-. In addition, one finds that the cis isomer aquates faster than the corresponding trans isomer for all cases expect NH_2^-, where, however, such a result has been postulated,[14] although still argued about.[15,16] If the metal center were to be changed to Cr(III), what trends would be seen? Our experiments and data in the literature give us the ability to answer this question.

The data for the aquation of Br^- from a number of Co(III) and Cr(III) amine systems are presented in Table III.[17-25]

In Figure 1 we examine the possibility of a linear free energy relationship between the rate of aquation of the Co(III) complexes and that of the Cr(III) complexes, including data for the base hydrolysis of $M(NH_3)_5Br^{2+}$.[19,20,26,27]

With regard to the activation parameter data, it is to be noted that the activation enthalpies parallel each other reasonably well (the values for Co(III) being somewhat more positive), with the exception of the *trans*-$M(en)_2OHBr^+$ complexes. The entropy of activation for all the Cr(III) substitutions are more negative than are those values for the Co(III) substitutions, in most cases substantially so. But the compensation between these two effects dulls a sharp difference in rate constant in most cases. The data shown in Figure 1 illustrate how this difference becomes manifest. Note that in the upper right of the figure the rate constant for Cr(III)

Table III. Kinetic Parameters for Bromide Aquation

	M = Co				M = Cr			
Complex	10^5k[a]	$\Delta H^{\ddagger b}$	$\Delta S^{\ddagger c}$	Ref	10^5k[a]	$\Delta H^{\ddagger b}$	$\Delta S^{\ddagger c}$	Ref
trans-$M(en)_2NCSBr^+$	0.05	29.5	9.5	17	3.2	25	5	18
$M(NH_3)_5Br^{2+}$	0.63	23.4	−4	19	10.3	19.9	−6.4	20
						21.8	−3.6	21
trans-$M(en)_2Br_2{}^+$	13.9	25.0	7.6	22	32.6	21.8	−1.4	9, 23
cis-$M(en)_2Br_2{}^+$	104	23.2	5	24	230	18.6	−8.3	25
trans-$M(en)_2OHBr^+$	950	24.4	14.1	22	5450	18.0	−4	This work
cis-$M(en)_2OHBr^+$	6000	22.7	11.7	22	4800	19.5	0.8	This work

[a] Units are s^{-1}. [b] Units are kcal mol^{-1}. [c] Units are cal mol^{-1} deg^{-1}.

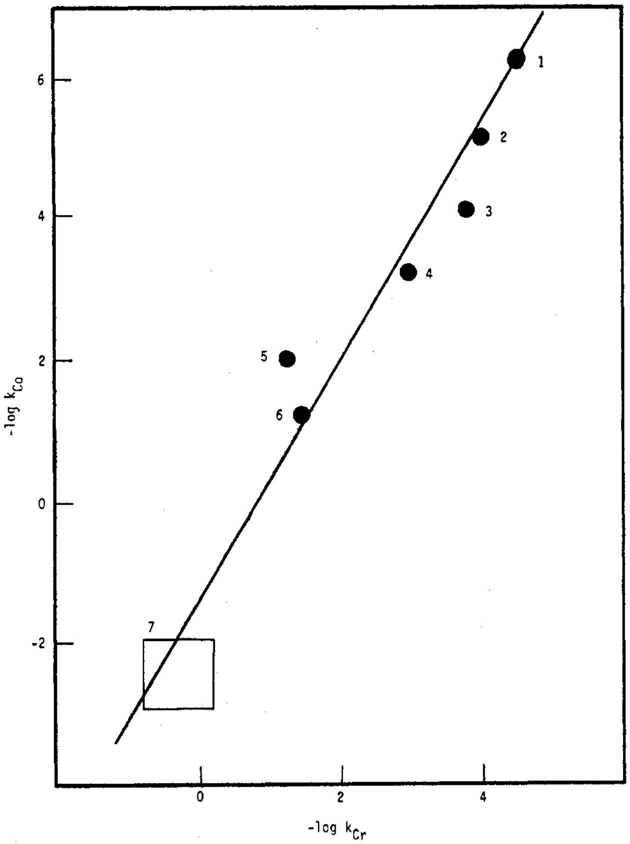

Figure 1. Linear free energy relationship of rate constants for aquation of Br^- from $M(L_4XBr^{n+})$ complexes. Points are (1) *trans*-$M(en)_2(NCS)Br^{n+}$, (2) $M(NH_3)_5Br^{2+}$, (3) *trans*-$M(en)_2Br_2^+$ corrected for statistical difference, (4) *cis*-$M(en)_2Br_2^+$ corrected for statistical difference, (5) *trans*-$M(en)_2(OH)Br^+$, (6) *cis*-$M(en)_2(OH)Br^+$, and (7) $M(NH_3)_4(NH_2)Br^+$ for the range of acidity constants of $M(NH_3)_5Br^{2+}$ of 10^{-15} to 10^{-16}.

complexes is considerably larger than those for Co(III) complexes, but by the point for *cis*-$M(en)_2OHBr^+$, the reverse order of rate constants prevails. The slope of the line drawn through these data is about 0.6, indicating this change in reactivity order.

We began this study anticipating that we would observe a change in slope in the curve in the figure. We reasoned that since $Cr(NH_3)_5Br^{2+}$ presumably substituted by an I_a pathway[1] and since the conjugate base path for this complex is presumably I_d,[1] then at some "directing" group intermediate in labilizing ability between NH_3 and NH_2^-, a mechanism change would occur. This change would cause a difference in slope. Clearly the data do not support the prediction.

There are three interpretations for the straight line behavior of the log–log plot and the value of the slope. If all of the Cr(III) and Co(III) aquations are assumed to be I_d and the activating pathway for these ligands is presumed to be their ability to π donate to relieve charge buildup in the dissociative transition state, then the lower demand for this donation in Cr(III), the least polarizing of the two cations, could account for the slope of less than 1. This view would presumably be endorsed by Ramasami and Sykes.[28] Alternatively, we could assume the mechanism for substitution at all the Cr(III) centers is associative interchange, whereas that at the Co(III) center is I_d. In this case the Cr(III) complexes have bond formation aiding in bond rupture and therefore have less requirement of charge supply by the "directing" groups. Thirdly, it is possible that both of the above mentioned phenomena are active, and the slopes generated by each coincide within the scatter caused by other properties of the complexes and the experimental error.

Registry No. *trans*-$Cr(en)_2OHBr^+$, 60933-53-1; *cis*-$Cr(en)_2OHBr^+$, 60886-01-3; *cis*-$[Cr(en)_2H_2OBr]Br_2$, 30172-32-8; *cis*-$[Cr(en)_2Cl_2]ClO_4$, 15654-71-4.

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An Accurate Redetermination of the Structure of Triruthenium Dodecacarbonyl, $Ru_3(CO)_{12}$

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We have recently determined the crystal structure of $H_2Os_3(CO)_{11}$ and have accurately redetermined ($R_F = 3.35\%$; 3040 reflections) the structure of the isomorphous species $Os_3(CO)_{12}$.[1] These results show (inter alia) that the axial Os–CO bonds in $Os_3(CO)_{12}$ are lengthened relative to the equatorial Os–CO linkages (average values are 1.946 (6) and 1.912 (7) Å, respectively). This result is completely in accord with the accepted model for M–CO bonding and occurs as a result of competition for d_π electron density between the (mutually trans) axial carbonyl ligands.

The published crystal structure of $Ru_3(CO)_{12}$[2] is of relatively low precision ($R_F = 7.9\%$; 936 reflections) and the reported Ru–CO bond lengths are such that the average Ru–CO (axial) distance of 1.89 (2) Å is slightly *shorter* than the average Ru–CO (equatorial) distance of 1.93 (2) Å.

As a result of this discrepancy, and with a firm belief that accurate molecular dimensions for all archetypal "binary"