hypersensitive transitions have been observed near 0.58 μ in $Nd_2Mg_3(NO_3)_{12} \cdot 24H_2O$.

The asymmetric site symmetry of the lanthanide ion in $Pr(NO_3)_3 \cdot 6H_2O$-type structures where there is a coordination to 10-oxygen atoms[10] may also be correlated with the existence of hypersensitive transitions. Observations by Selwood,[25] which we have confirmed, show clear hypersensitivity of the 0.58-μ band in $Nd(NO_3)_3 \cdot 6H_2O$. Infrared studies confirm the strongly covalent character of the nitrate groups in this class of compounds.[26]

Finally, it is instructive to compare the spectra of the Nd^{3+} ion in the previously discussed nitrate salts with that of Nd^{3+}: LaF_3, Figure 2. In this case, the site symmetry is again low, C_2,[27] but the spectrum is "normal;" *i.e.*, the intensity of the 0.58-μ band is similar to that observed for $Nd^{3+}(aq)$.[21,28,29] Since C_2 symmetry is included in the group which Judd identified with hypersensitive transitions, we may conclude, as Bukietynska and Choppin[30] have suggested, that symmetry may be a necessary but not a sufficient condition to the existence of hypersensitive transitions. In the case of $K_3Nd_2(NO_3)_9$ and the other crystalline salts discussed here, the correlation between strong covalent bonding of the lanthanide ion and the existence of intensity enhancement was indicated.

Registry No. $K_3Pr_2(NO_3)_9$, 37209-71-5; $K_3Nd_2(NO_3)_9$, 37209-70-4; $K_3Sm_2(NO_3)_9$, 37209-72-6; $K_2Er(NO_3)_5$, 37248-54-7.

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Kinetics of the Reduction of Cobalt(III) and Chromium(III) Complexes by Ytterbium(II) Ions[1a]

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Generation of solutions of Yb^{2+} in dilute perchloric acid was accomplished electrochemically. The Yb^{2+} solutions thus produced underwent solvent reduction over 10–30 min in the absence of oxygen but were sufficiently stable to permit kinetic studies on the reduction of some Co(III) and Cr(III) complexes. Measurements were made for $Co(NH_3)_6{}^{3+}$, $Co(en)_3{}^{3+}$, and $Co(NH_3)_5H_2O^{3+}$, as well as for halide and pseudohalide complexes of the series $Cr(NH_3)_5X^{2+}$ and $Cr(H_2O)_5X^{2+}$. The effects of $[H^+]$ and $[Cl^-]$ were examined for some reactions, as was the effect of temperature. The results are interpreted in terms of inner-sphere and outer-sphere mechanisms for different reactions.

Introduction

The reduction of metal complexes by one-electron reducing agents has occupied an important position in the field of inorganic reaction mechanisms ever since the original studies of Taube and coworkers[2] demonstrating the inner-sphere (IS) mechanism for certain Cr^{2+} reactions. Since that time, the IS mechanism has been found to be a rather general one for appropriately constituted 1-equiv reducing agents.[3,4] For many reducing agents, however, the mechanism for electron transfer cannot be inferred as directly as in Cr^{2+} reductions, for which the transfer and capture of the bridging group X as the Cr(III) complex can be established. In some other cases, especially V^{2+} [5] and Fe^{2+},[6] X transfer could also be demonstrated unequivocally. Even for these cases, the proof for an IS mechanism in certain reactions by no means establishes this as a general mechanism. Thus for many of the reactions of V^{2+} [3,7] and Fe^{2+} [7a,8] and for virtually all of the related redox reactions of Cu^+,[9] U^{3+},[10] and Eu^{2+},[7a,11] what conclusions can be drawn about the most elementary aspect of the mechanism—whether or not the structure of the transition state involves a bridging group—can be approached only by a very indirect means.

It thus seemed of some interest to attempt studies which would extend the number of reducing agents, because such

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comparisons have proved fruitful in earlier work. Particulary, since Eu^{2+} was the only lanthanide ion among the reducing agents, we decided to examine certain reactions of divalent ytterbium. Because Yb(II) is an exceptionally powerful reducing agent, as shown by

$$\mathrm{Yb^{3+} + e^- = Yb^{2+}} \quad E^\circ = -1.15\ \mathrm{V}[12] \tag{1}$$

the complication arises that reduction of water and hydrogen ions to $H_2(g)$ is the most important factor in deciding the stability of solutions of $Yb_{aq}{}^{2+}$. Our observations with regard to the rate of solvent reduction by this ion are in accord with those made by a number of earlier workers[13] and stand in marked contrast to the extremely rapid disappearance of Yb^{2+} recently reported by Faraggi and Tendler.[14] We shall consider this disagreement later. Adamson[13a] did find that decomposition occurred sufficiently rapidly to prevent kinetic studies on the Yb^{2+}-Yb^{3+} isotopic exchange reaction.

The oxidations of Yb(II) by the Co(III) and Cr(III) complexes employed in this study were rapid enough that the spontaneous solvent oxidation was insignificant in determining the overall reaction rate but remained of importance in preparing and handling Yb(II) solutions.

In the present work the solutions of Yb(II) were prepared by electrochemical reduction of $Yb(ClO_4)_3$ at a mercury electrode. Kinetic investigations were carried out on certain complexes of Co(III)[15] and Cr(III) with the goal of exploring the reaction mechanisms followed in these cases and in comparison to similar reactions of Eu(II).

Experimental Section

Materials. Literature methods were employed for the preparation of the following complexes: $Co(en)_3Cl_3$,[16a] $Co(NH_3)_6Cl_3$,[16b] $[Co(NH_3)_5OH_2](ClO_4)_3$,[17] $[Cr(NH_3)_5OH_2](ClO_4)_3$,[18] $[Cr(NH_3)_5F]F_2$,[19] $[Cr(NH_3)_5Cl]Cl_2$,[20] and $[Cr(NH_3)_5Br]Br_2$.[21] $[Cr(NH_3)_5Br]Br_2$ was recrystallized from aqueous solution with NaBr and was used, as the bromide salt, for the rate measurements. All the other halide salts were converted to the corresponding perchlorate salts by recrystallization from dilute perchloric acid solutions (50% aqueous ethanol being required for the precipitation of $Co(en)_3(ClO_4)_3$). In all cases, the recrystallations were continued until the ratio of absorbance maximum to minimum no longer changed. The spectra of the pure products were found to be in good agreement with the literature.[17,22-26]

The chromium(III) complexes of the general formula $Cr(H_2O)_5X^{2+}$ were obtained in solution, the complexes being purified by ion-exchange chromatography on a Dowex 50W-X8 column using 1 *F* perchloric acid to elute the desired material. The preparations of the individual complexes were as follows. The complex $CrCl^{2+}$ was prepared by treating $CrCl_3 \cdot 6H_2O$ with a small amount of Cr^{2+}.[27,28] The bromo complex was obtained from the reaction of chromium(II) and bromine.[29] The complexes $CrNCS^{2+}$, CrF^{2+}, and $CrN_3{}^{2+}$ were prepared by anation reactions as described in the literature.[30,31]

Stock solutions of $Yb(ClO_4)_3$ were prepared from the reaction of Yb_2O_3 with excess perchloric acid; the typical stock solution had final concentrations 0.05 *F* $Yb(ClO_4)_3$ and 0.05 *F* $HClO_4$ and was diluted considerably before reduction to Yb(II).

Yb(II) Solutions. Solutions of Yb(II) were prepared only for immediate use owing to its reasonably rapid reduction of water. Most solutions contained *ca.* 10^{-2} *M* H^+, but in some instances other acid concentrations were used. Generation of Yb(II) was accomplished by electrochemical reduction at a mercury cathode. Nitrogen purified by bubbling through Cr^{2+} solutions was used to purge the solutions throughout. For experiments using the Cary spectrophotometer, the Yb^{2+} solutions were removed from the preparation vessel by a syringe with a long Teflon needle and injected directly into the reaction cell containing all the other reagents. The reaction cell in this instance consisted of a cylindrical quartz tube[32] approximately 25 mm in diameter, immersed in a thermostating bath in the cell compartment of the spectrophotometer. The solutions were mixed by a stream of nitrogen, and after mixing the bubbling tube was withdrawn to just above the surface of the solution.

For the stopped-flow experiments an inlet tube led directly from the solution reservoir into one drive syringe of the stopped-flow apparatus. The kinetic experiments were performed as quickly as possible to minimize loss of Yb(II) to solvent reduction.

The efficiency of the reduction process was such that typically 30-70% of the Yb(III) was converted to Yb(II), although this depended upon the time allowed for the electrolysis as well as the hydrogen ion concentration.

A few measurements were made to estimate the rate of decomposition of Yb^{2+} in perchloric acid solutions according to

$$\mathrm{Yb^{2+} + H^+ = Yb^{3+} + \tfrac{1}{2}H_2(g)} \tag{2}$$

The decomposition proceeded slowly, and as a consequence reproducible rate data were difficult to obtain; slow leakage of air and/or reaction with oxidizing impurities may have been responsible for part of the observed decrease in $[Yb^{2+}]$, and consequently the rates cited are upper limits on reaction 2. The decomposition rate was expressed in terms of $-d \ln [Yb^{2+}]/dt$, although the adherence to a pseudo-first-order rate expression was not verified in detail; values of 3.5, 0.8, 1.3, and 0.8 (in units $sec^{-1} \times 10^4$ at 21-24°) were obtained in the media 0.009 *F* $HClO_4$ and 0.061 *F* $LiClO_4$, 0.015 *F* $HClO_4$ and 0.93 *F* $LiClO_4$, and 0.94 *F* $HClO_4$ and 0.95 *F* HCl, respectively. These results establish the general range of decomposition rates, showing that reaction 2 will not interfere with the kinetic studies on Co(III) and Cr(III) complexes except in the case of very slow reactions.

These experiments can be compared to the very rapid decay rate found by Faraggi.[14] In the very dilute ($\sim 10^{-6}$-10^{-5} *M*) solutions of Yb^{2+} in the presence of 0.01 *M* Yb^{3+} and 0.01 *M* CH_3OH (to scavenge OH radicals which otherwise oxidize Yb^{2+} very rapidly), they reported a pseudo-first-order rate constant of $90 \pm 10\ sec^{-1}$ ($t_{1/2} = 7.7$ msec) at pH 2.4-6.5. Moreover, they found that the decomposition rate increased with $[Yb^{3+}]$, suggesting a more complicated mechanistic pathway than indicated by eq 2 involving two ytterbium atoms.

Under conditions similar to those where Faraggi and Tendler reported this rapid 7.7-msec decomposition, we find a half-time for decay of ~30 min. The longer lifetimes also appear more consistent with other results. Adamson,[13a] for example, found a half-time of *ca.* 10 min for the decay in 1 *F* HCl, and Ball[13d] noted that about 15 min is required for the color of Yb(II) to fade in HCl solution. Butement[13b] noted that 1 hr is required to complete the decomposi-

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tion of 0.01 *F* $YbCl_2$ in 0.1 *F* HCl. There seems little doubt that the rapid decay rate found by Faraggi and Tendler[14] corresponds to a stoichiometric process other than eq 2 and is one that is unique to their work.

On the other hand, the spectrum of Yb(II) they reported[14] agrees with that given by other workers[13] as do our results. Yb(II) has an absorption maximum at λ 352 nm (ϵ *ca.* 600 M^{-1} cm^{-1}). This peak proved a convenient one for monitoring the spectral changes both in the decomposition process as well as in the kinetic runs. The uv peak for Yb^{2+} at λ 246 nm (ϵ *ca.* 1300) was used for a few runs without noting appreciable differences.

We suggest that a possible reason for the rapid decay found in Faraggi and Tendler's work arises from the use of extremely dilute Yb(II) solutions which are then exceptionally sensitive to impurities. This view is supported by the fact that the decomposition rate is proportional not just to $[Yb^{2+}]$, but to the product $[Yb^{2+}][Yb^{3+}]$, the trivalent ion being present in very great excess. This suggests to us the possibility that the commercial $Yb_2(SO_4)_3$ might contain an oxidizing impurity which is responsible for their fast decay reactions and which would account for an apparent dependence upon the Yb(III) concentration.

Kinetics Experiments. The reaction rates in most cases were determined by the stopped-flow method using an apparatus of the design of Dulz and Sutin.[33] In the case of slower reactions the measurements were made using a Cary Model 14 spectrophotometer.

In most experiments the concentration conditions were such that the oxidizing agent was in excess over $[Yb^{2+}]_0$ by a factor of 10 or more. Under such circumstances the reaction followed pseudo-first-order kinetics. In a few runs comparable concentrations of Yb^{2+} and oxidizing agent were employed. Plots of log $\{[M(III)]/[Yb^{2+}]\}$ *vs.* time proved to be linear in these runs and led to values of k_2 in agreement with those from the pseudo-first-order determinations. The initial concentration of Yb^{2+} in such experiments was determined by analysis of each separate reaction solution for the yield of Co^{2+}.

For certain of the Cr(III) complexes it was necessary to take precautions to avoid aquation of the halide group prior to reaction. For $Cr(NH_3)_5Br^{2+}$, for example, the aquation rate is sufficiently high (5% reaction in ~8.5 min at 25° and in ~25 min at 15.8°[24]) that studies were restricted to the lower temperature. Stock solutions were made up at 0° and brought to 15.8° only shortly before reaction was begun. Likewise, solutions of $CrBr^{2+}$ were used within a short time of ion-exchange separation because the aquation time is also reasonably rapid (5% reaction in ~180 min at 25° with $[H^+] = 1\,M$[29]).

Results

Stoichiometry. The reactions of the Yb(II) with Co(III) complexes were presumed to proceed as shown in eq 3 for

$$Co(NH_3)_6{}^{3+} + Yb^{2+} + 6H^+ = Co^{2+} + Yb^{3+} + 6NH_4{}^+ \qquad (3)$$

$Co(NH_3)_6{}^{3+}$. The Co(II) in the product solutions was determined spectrophotometrically as the thiocyanate complex in aqueous acetone.[34] The spectra of the product solutions also supported the production of Yb^{3+}.

Control of the Reaction Medium. The initial kinetic studies were carried out on the reaction of $Co(en)_3{}^{3+}$ and Yb^{2+}, with ionic strength maintained at a constant value of 0.20 by addition of the 1:1 electrolyte $LiClO_4$ and concentrations of $[Co(en)_3](ClO_4)_3$ in the range 0.0023-0.015 *M*. The value of the second-order rate constant decreased regularly from 548 to 451 M^{-1} sec^{-1} with increasing $[Co(en)_3{}^{3+}]$. Although the variation might be attributed to a more complicated rate expression, an alternative explanation was sought in the variation of the reaction medium. Olson and Simonson[35] have found that medium effects on the rate constant for the reaction of two multiply charged *cations* are controlled by constant *anion* concentration. A series of experiments was subsequently carried out in which $[ClO_4^-]$ as well as ionic strength was maintained constant.

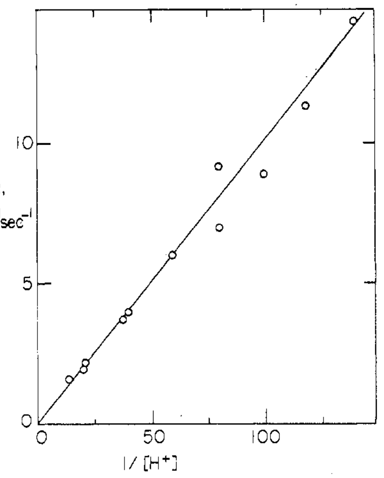

Figure 1. A plot of the apparent second-order rate constant for the reaction of $Cr(H_2O)_6{}^{3+}$ and Yb^{2+} *vs.* $1/[H^+]$.

Similarly, $La(ClO_4)_3$ was added to the solutions of $Cr(H_2O)_6{}^{3+}$ and $Co(NH_3)_6{}^{3+}$. In the case of $Co(NH_3)_5H_2O^{3+}$ the much lower cobalt concentration employed did not require the added 3:1 electrolyte, and the ionic strength was maintained at 0.200 *M* by addition of lithium perchlorate only.

The reaction of $Cr(NH_3)_5X^{2+}$ and $Cr(H_2O)_5X^{2+}$ complexes was studied in a medium containing added $Ba(ClO_4)_2$ and $LiClO_4$. The medium had $\mu_{2+} = 0.100\,M$ and $\mu_T = 0.200\,M$ to achieve the simultaneous constancy of ionic strength and perchlorate concentration.

Kinetics. The kinetic data on Co(III) and Cr(III) complexes are presented in Table I. The variation of M(III) concentration in each case (except $CrNCS^{2+}$) was sufficient to confirm strict adherence to a second-order rate expression. The studies in every case encompassed a range of hydrogen ion concentrations, usually in the range 0.005-0.10 *M*, it being difficult to prepare Yb^{2+} solutions at higher $[H^+]$. Each of these complexes reacted at a rate independent of $[H^+]$.

The kinetic studies of $Cr(H_2O)_5NCS^{2+}$ were not reproducible, and did not give results in accord with the second-order rate expression. Several attempts were made at independent preparations and purifications, but this did not improve the situation. The values of k_2 ranged from *ca.* 2 to 7 M^{-1} sec^{-1}, and tended to be larger at higher $[CrNCS^{2+}]$. Decay of Yb(II) in these slower reactions may be responsible for the irreproducibility.

The only exception to the lack of dependence on $[H^+]$ is provided by $Cr(H_2O)_6{}^{3+}$, for which the kinetic data are listed in Table II. A plot of k_2 *vs.* $[H^+]^{-1}$ is linear with zero intercept, as depicted in Figure 1. The rate equation is

$$\frac{-d[Cr^{3+}]}{dt} = k\frac{[Cr(H_2O)_6{}^{3+}][Yb^{2+}]}{[H^+]} \qquad (4)$$

where $k = k_2[H^+]$ and has the value 0.101 ± 0.007 sec^{-1} at 25.0° and $\mu = 0.200\,M$.

Rate measurements were also attempted on the reaction of Yb^{2+} with $Co(NH_3)_5X^{2+}$ complexes for $X^- = OAc^-$, and $-NCS^-$. The rate constant for the acetate complex is ~3 × 10^5 M^{-1} sec^{-1}, and for the isothiocyanate complex, where the reaction was complete upon mixing even at very low concentrations, we set the limit $k > 10^6\ M^{-1}\ sec^{-1}$.

There is also a lower limit of rates that can be studied. The reduction of $Cr(NH_3)_5H_2O^{3+}$ by Yb^{2+} is one such case.

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Table I. Kinetic Data for the Reduction of Co(III) and Cr(III) Complexes by Yb(II)[a]

$[Co^{III}]$, M x 10^3	$[H^+]$, M	$10^n k_2$, M^{-1} sec^{-1}
$Co(en)_3^{3+}$[b], 25.0°, n=-2		
2.12	0.0050	4.41±0.05
2.31	0.051	4.37±0.07
4.03	0.0050	4.61±0.02
4.16	0.010	4.36±0.06
4.18	0.051	4.59±0.06
7.51	0.0050	4.32±0.11
9.76	0.0050	4.40±0.14
10.71	0.010	4.54±0.26
12.61	0.010	4.45±0.13
15.01	0.0050	4.43±0.27
$Co(NH_3)_6^{3+}$[b], 25.0°, n=-3		
0.545	0.0060	2.36±0.06
0.556	0.023	2.32±0.13
1.02	0.023	2.36±0.10
1.07	0.0028	2.08±0.04
1.53	0.023	2.20±0.05
1.73	0.0056	2.19±0.05
2.05	0.023	2.21±0.07
2.17	0.0113	2.16±0.05
2.28	0.0028	2.11±0.02
2.44	0.011	2.31±0.07
2.45	0.011	2.32±0.04
2.54	0.0050	2.23±0.07
2.56	0.056	2.26±0.04
3.07	0.023	2.22±0.05
3.31	0.0060	2.21±0.06
3.56	0.0090	2.28±0.05
3.81	0.0056	2.11±0.08
4.01	0.023	2.31±0.05
$Co(NH_3)_5H_2O^{3+}$[c], 25.0°, n=-4		
0.296	0.023	2.94±0.05
0.317	0.023	2.92±0.15
0.423	0.197	3.04±0.14
0.459	0.0020	3.40±0.04
0.492	0.068	3.20±0.17
0.559	0.090	3.10±0.14
0.567	0.090	2.74±0.09
0.599	0.082	3.05±0.15
0.700	0.045	3.38±0.16
0.708	0.099	3.51±0.26
1.08	0.023	3.36±0.29

$[Cr^{III}]$, M x 10^3	$[H^+]$, M	$10^n k_2$, M^{-1} sec^{-1}
$Cr(NH_3)_5F^{2+}$[d], 15.8°, n=-1		
9.30	0.010	4.02±0.11
$Cr(NH_3)_5F^{2+}$[d], 25.0°, n=-1		
2.82	0.010	5.42±0.06
5.03	0.100	5.94±0.24
5.33	0.013	5.55±0.32
10.0	0.013	5.41±0.19
14.9	0.047	5.39±0.05
20.1	0.013	5.26±0.08
$Cr(NH_3)_5Cl^{2+}$[d], 15.8°, n=0		
0.733	0.017	9.65±0.06
1.36	0.017	9.11±0.16
2.40	0.008	9.74±0.20
10.3	0.013	9.34±0.46
19.7	0.013	9.65±0.19
$Cr(NH_3)_5Cl^{2+}$[d], 25.0°, n=-1		
5.37	0.013	1.34±0.03
8.02	0.047	1.40±0.11
9.77	0.100	1.43±0.03
10.9	0.0060	1.33±0.04
12.3	0.010	1.44±0.05
19.4	0.013	1.24±0.05
31.8	0.013	1.33±0.03
$Cr(NH_3)_5Br^{2+}$[d], 15.8°, n=-1		
0.655	0.041	1.59
0.697	0.040	1.54±0.09
1.02	0.017	1.42
1.14	0.0080	1.41
1.26	0.040	1.53±0.05
1.55	0.040	1.45±0.04
1.76	0.088	1.27
1.88	0.094	1.26
1.96	0.100	1.35
1.97	0.040	1.42±0.02
2.10	0.040	1.35±0.03
2.63	0.032	1.30
3.46	0.040	1.36
3.62	0.040	1.33

$[Cr^{III}]$, M x 10^3	$[H^+]$, M	$10^n k_2$, M^{-1} sec^{-1}
$Cr(H_2O)_5F^{2+}$[d], 25.0°, n=-3		
5.00	0.0254	2.09±0.09
5.00	0.0330	1.89±0.13
5.00	0.0400	2.01±0.13
7.50	0.0347	1.87±0.10
10.0	0.0441	1.87±0.07
$Cr(H_2O)_5Cl^{2+}$[d], 25.0°, n=-3		
10.0	0.030	1.00±0.03
10.0	0.040	1.05±0.07
10.0	0.050	0.96±0.01
$Cr(H_2O)_5Br^{2+}$[d], 25.0°, n=-3		
4.00	0.0532	1.65±0.05
4.00	0.0652	1.66±0.04
6.00	0.0745	1.70±0.09
8.00	0.0973	1.60±0.08
$Cr(H_2O)_5N_3^{2+}$[d], 25.0°, n=-3		
2.34	0.0041	4.54±0.29
2.93	0.0142	3.47±0.59
2.93	0.0243	3.77±0.30
3.08	0.0041	5.04±0.19
4.33	0.0041	4.73±0.28
5.77	0.0041	4.72±0.11
5.77	0.0500	4.72±0.16
7.20	0.0041	4.68±0.28
$Cr(H_2O)_5NCS^{2+}$[d], 25.0°, n=0		
5.2	0.0864	1.96±0.02
5.3	0.0490	3.52±0.08
5.3	0.0490	3.81±0.00
5.3	0.0744	2.88±0.04
5.6	0.0490	2.28±0.12
7.0	0.0864	2.26±0.03
8.0	0.0490	4.39±0.10
8.4	0.0854	7.1 ±1.0
10.6	0.0490	5.12±0.03
11.2	0.0854	6.7 ±0.3

[a] The uncertainty for each rate constant represents the average deviation from the mean of two to four repeat determinations; the initial $[Yb^{2+}]$ was typically (1–6) × 10^{-4} *M*. [b] $\mu_T = 0.178\,M$, $\mu_{3+} = 0.078\,M$. [c] $\mu_T = 0.200\,M$, univalent ions only. [d] $\mu_T = 0.200\,M$, $\mu_{2+} = 0.100\,M$.

Table II. Kinetic Data for the Reaction of $Cr(H_2O)_6^{3+}$ and Yb(II) at 25.0°[a]

Initial concn, *M*		k_2, M^{-1} sec^{-1}	$k = k_2[H^+]$, sec^{-1}
$[Cr(H_2O)_6^{3+}]$	$[H^+]$		
0.0141	0.0072	14.3	0.103
0.0085	0.00833	11.3	0.094
0.0085	0.0100	8.85	0.089
0.0071	0.0125	9.14	0.114
0.0085	0.0125	6.97	0.087
0.0085	0.0167	6.00	0.100
0.0085	0.0250	3.96	0.099
0.0141	0.0265	3.70	0.098
0.0075	0.0489	2.15	0.105
0.0141	0.0489	2.11	0.103
0.0085	0.0500	1.95	0.098
0.0141	0.0744	1.60	0.119
		Av	0.101 ± 0.007

[a] With $\mu_T = 0.20\,M$ and $\mu_{3+} = 0.10\,M$; followed at λ 350 nm.

Under the concentration conditions $[Cr(NH_3)_5H_2O^{3+}] = 0.015\,M$ and $[Yb^{2+}]_0 \approx 6 \times 10^{-4}\,M$ at $[H^+] = 0.04\,M$, only a very slow decrease in the absorbance at 350 nm was noted when the reaction was followed using the Cary spectrophotometer, which was largely the decomposition process of eq 2 rather than reduction of the Cr(III) complex. The upper limit on the rate constant for the reaction of $Cr(NH_3)_5 \cdot H_2O^{3+}$ and Yb^{3+} is $k_2 < 0.02\,M^{-1}\,sec^{-1}$.

The average rate constants for each complex are summarized in Table III. In addition to those values and the results given in Table I, the following complexes were studied at other temperatures: $Co(en)_3^{3+}$: $10^{-2}k_2$ (M^{-1} sec^{-1}) = 3.94 ± 0.08 (15.8°), 4.07 ± 0.03 (20.4°), 4.49 ± 0.03 (29.6°), 4.99 ± 0.17 (34.2°), 4.95 ± 0.18 (38.8°); $Co(NH_3)_6^{3+}$: $10^{-3}k_2$ (M^{-1} sec^{-1}) = 2.05 ± 0.03 (15.8°), 2.49 ± 0.02 (34.2°). Activation parameters for the four complexes for which temperature-dependence studies were done are summarized in Table IV.

Anion Effects. A number of rate measurements were also made with free chloride ions added. For the Co(III) complexes a catalytic effect of Cl^- was quite evident. The effect is linear in $[Cl^-]$ according to the relation

$$k_{app} = k_2 + k_{Cl}[Cl^-] \qquad (5)$$

Table III. Summary of Rate Constants for the Reduction of Co(III) and Cr(III) Complexes by Yb(II)[a]

Complex	k_2, M^{-1} sec^{-1} (no. of expts)[b]
$Co(en)_3{}^{3+}$	$(4.45 \pm 0.15) \times 10^2$ (10)
$Co(NH_3)_6{}^{3+}$	$(2.23 \pm 0.09) \times 10^3$ (11)
$Co(NH_3)_5H_2O^{3+}$	$(3.14 \pm 0.26) \times 10^4$ (11)
$Cr(NH_3)_5F^{2+}$	(55.0 ± 2.5) (6)
$Cr(NH_3)_5Cl^{2+}$	(13.5 ± 0.7) (5)
$Cr(NH_3)_5Br^{2+}$	(14.2 ± 0.8) (22)[c]
$Cr(H_2O)_5F^{2+}$	$(1.95 \pm 0.08) \times 10^3$ (5)
$Cr(H_2O)_5Cl^{2+}$	$(1.00 \pm 0.03) \times 10^3$ (3)
$Cr(H_2O)_5Br^{2+}$	$(1.65 \pm 0.03) \times 10^3$ (4)
$Cr(H_2O)_5N_3{}^{2+}$	$(4.46 \pm 0.42) \times 10^3$ (8)
$Cr(H_2O)_5OH^{2+}$	$(7.8 \pm 0.5) \times 10^2$ (12)[d]

[a] The concentration range covered for each complex is given in Table I; rate constants refer to 25.0° except as noted. [b] The uncertainty given for each rate constant represents the average deviation from the mean of the number of independent determinations given in parentheses. [c] 15.8°. [d] Computed from k values (Table II) and K_a for $Cr(H_2O)_6{}^{3+}$ as described in the text.

Table IV. Activation Parameters[a]

Complex	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, cal mol^{-1} K^{-1}
$Co(en)_3{}^{3+}$	1.3 ± 0.2	-42.1 ± 0.6
$Co(NH_3)_6{}^{3+}$	1.3 ± 0.2	-38.9 ± 0.6
$Cr(NH_3)_5F^{2+}$	5.2 ± 0.5	-33.2 ± 1.8
$Cr(NH_3)_5Cl^{2+}$	5.7 ± 0.4	-34.4 ± 1.3

[a] The indicated uncertainty is the standard deviation.

where k_2 is the rate constant in the absence of Cl^-. Figure 2 depicts a plot of k_{app}/k_2 *vs.* $[Cl^-]$. The slopes of these lines result in the following values of k_{Cl} (M^{-2} sec^{-1}) at 25.0°: $Co(en)_3{}^{3+}$, $(5.03 \pm 0.11) \times 10^3$; $Co(NH_3)_6{}^{3+}$, $(2.00 \pm 0.06) \times 10^4$; $Co(NH_3)_5H_2O^{3+}$, $(1.62 \pm 0.12) \times 10^5$.

The rate constants for the $Cr(NH_3)_5X^{2+}$ complexes, on the other hand, are independent of $[Cl^-]$ to the highest value studied, 0.1 M.

Interpretation and Discussion

The complexes $Co(NH_3)_6{}^{3+}$ and $Co(en)_3{}^{3+}$ react, of necessity, by the outer-sphere (OS) mechanism. The significant catalysis by Cl^- supports this assignment, and it appears to constitute one characteristic feature of this mechanism.[10,36-38] The reaction of $Co(NH_3)_5H_2O^{3+}$ appears to follow the same OS mechanism, a conclusion drawn from two observations, a catalytic effect by Cl^- comparable to that for known OS reactions and the lack of a kinetic dependence on $[H^+]$.[39,40] The latter constitutes an observation that is now regarded as a reliable criterion for the OS reaction mechanism.[9a,10,11b,36-38,41]

The reactions of the three Co(III) complexes constitute a close parallel to the same reactions of Eu^{2+}.[7a,38,42] Our conclusions also parallel those of Sykes. To the best of our knowledge a study of the anion catalysis has not been carried out for the Eu^{2+} reactions, but it seems highly likely that those reactions would also show strong catalysis by free anions.

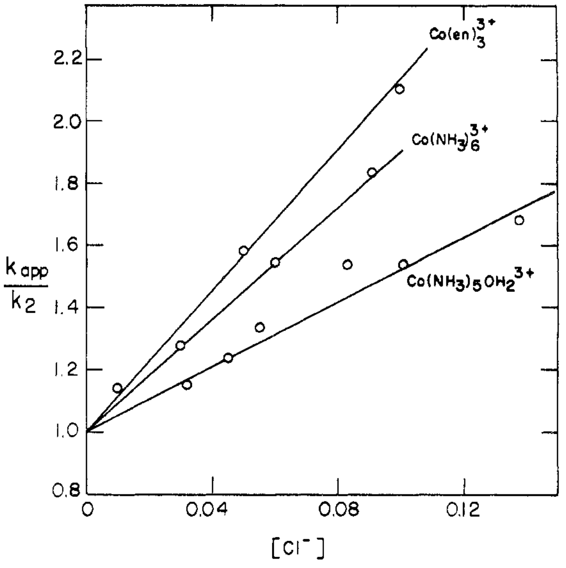

Figure 2. The linear variation with $[Cl^-]$ of the ratio of the apparent second-order rate constant to the value of k_2 at $[Cl^-] = 0$ for three Co(III) complexes.

The role of Cl^- may be attributed to either of two likely mechanisms: the reaction of the ion pair $ML_6{}^{3+}, Cl^-$ with Yb^{2+}, or the reaction of $ML_6{}^{3+}$ with $YbCl^+$. No kinetic test will distinguish the two possibilities because both possible Cl^- preequilibria are "instantaneous." Nevertheless, arguments based on anticipated values of the bimolecular rate constants computed for each alternative suggest the former may be a better formulation.[43]

More important, however, is the question of the role which Cl^- plays and its structural position in the activated complex. For Yb^{2+} the question cannot be answered directly, but for Cr^{2+} reactions the anion pathway generates $CrCl^{2+}$ suggesting the structure $[ML_6{}^{3+}, Cl^- \text{-} Cr(OH_2)_5{}^{2+}]^{\ddagger}$. This would correspond to a "pseudo-inner-sphere" process.

The reactions of the Cr(III) complexes stand in contrast to the Co(III) reactions in certain respects. The former reactions proceed without catalysis by free Cl^-, and a rather marked rate enhancement for $CrN_3{}^{2+}$ over $CrNCS^{2+}$ was noted (although accurate data were not obtained for the latter complex). These results suggest an IS reaction, although the evidence is not compelling.

The results on the reaction of $Cr(H_2O)_6{}^{3+}$ with Yb^{2+} are likewise suggestive of the IS mechanism. The rate dependence on $[H^+]^{-1}$ is in accord with the mechanism

$$Cr(H_2O)_6{}^{3+} \rightleftharpoons Cr(H_2O)_5OH^{2+} + H^+ \quad K_a \tag{6}$$

$$Cr(H_2O)_5OH^{2+} + Yb^{2+} \rightarrow Cr(II) + Yb(III) \quad k' \tag{7}$$

according to which $k' = k/K_a$. Using the value $K_a = 1.3 \times 10^{-4}$ M at 25.0° and $\mu = 0.20 M$[40] the bimolecular rate constant for reaction 7 is computed as 7.8×10^2 M^{-1} sec^{-1}. This value is comparable to that obtained for other $Cr(H_2O)_5X^{2+}$ complexes, which is the result expected for the IS mech-

(36) A. Zwickel and H. Taube, *Discuss. Faraday Soc.*, **29**, 72 (1960).

(37) J. F. Endicott and H. Taube, *J. Amer. Chem. Soc.*, **86**, 1686 (1964).

(38) J. Doyle and A. G. Sykes, *J. Chem. Soc. A*, 2836 (1968).

(39) In more quantitative terms we set a limit in the reactivity of $Co(NH_3)_5OH^{2+}$ relative to that of $Co(NH_3)_5H_2O^{3+}$ as $k_{OH}/k_{H_2O} < 5 \times 10^2$. This value is based on the value $K_a = 6.6 \times 10^{-7}$ M for the aquo complex,[40] and it assumes that as much as a 20% contribution from the hydroxo complex might have gone undetected at the lowest $[H^+]$, 0.002 M.

(40) The value of K_a for $Co(NH_3)_5H_2O^{3+}$ is given by R. G. Splinter, S. J. Harris, and R. S. Tobias, *Inorg. Chem.*, **7**, 897 (1968); The extrapolation to 0.20 M ClO_4^- was made assuming the same dependence upon ionic strength as shown by K_a for $Cr(H_2O)_6{}^{3+}$. [C. Postmus and E. L. King, *J. Phys. Chem.*, **59**, 1208 (1957).]

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

(42) The independent data for Eu^{2+} on the two complexes $Co(NH_3)_6{}^{3+}$ and $Co(NH_3)_5H_2O^{3+}$ are not in particularly good agreement as to the magnitude of the rate constants, but the general patterns agree. Sykes and coworkers[39] found values of k_2 which are lower than Halpern's by a factor of 12 for the former complex and a factor of 2 for the latter. Only Halpern[7a] has given data for $Co(en)_3{}^{3+} + Eu^{2+}$.

(43) D. W. Carlyle and J. H. Espenson, *Inorg. Chem.*, **8**, 575 (1969).

anism. The reaction of Eu^{2+} and $Cr(H_2O)_6{}^{3+}$ was not studied as a function of $[H^+]$.[44]

The approach suggested by Haim[45] was used to consider the unusual halide reactivity order of $Cr(H_2O)_5X^{2+}$ complexes. The stability constant[46-51] for each complex was used to compute the relative stability of each transition state $[(H_2O)_5Cr\text{-}X\text{-}Yb_{aq}{}^{4+}]^{\ddagger}$, as summarized in Table V. The stability order is F $\gg$ Cl > Br, supporting the IS mechanism.

The stability constants for the three $Cr(NH_3)_5X^{2+}$ complexes do not appear to be known with sufficient precision to permit the same computation in this case. There is little doubt based on reasonable estimates, however, that the same ordering of transition-state stabilities would result in this case also.

Application of the Marcus relation[51,52] to the OS reactions of the Co(III) complexes was attempted.[53] The rate constant for the "cross reaction" is given by

$$k_{12} = (k_{11}k_{22}K_{12}f)^{1/2} \tag{8}$$

where the symbols assume their usual meanings. The quantities needed for the direct application of this relation are not known, but division of two such relations, one for Yb(II)-Co(III) reaction and the other for Eu(II)-Co(III), yields the expression

$$\frac{k_{\mathrm{YbCo}}}{k_{\mathrm{EuCo}}} = \left(\frac{k_{\mathrm{Yb}}}{k_{\mathrm{Eu}}}\right)^{1/2} \left(\frac{K_{\mathrm{YbCo}}}{K_{\mathrm{EuCo}}}\right)^{1/2} \tag{9}$$

Table V. Stability of Cr–Yb Transition States

	K_X,[a] M^{-1}	Rel stability[b] of $[(H_2O)_5CrXYb_{aq}{}^{4+}]^{\ddagger}$
$Cr(H_2O)_5OH^{2+}$	1.3×10^{10} [c]	2.8×10^{12}
$Cr(H_2O)_5F^{2+}$	1.7×10^{4} [d]	9.1×10^{6}
$Cr(H_2O)_5N_3{}^{2+}$	$\sim 1 \times 10^{3}$ [e]	1.2×10^{6}
$Cr(H_2O)_5NCS^{2+}$	1.7×10^{2} [f]	$\sim 10^{2}$
$Cr(H_2O)_5Cl^{2+}$	8×10^{-2} [g]	2.2×10
$Cr(H_2O)_5Br^{2+}$	2.2×10^{-3} [h]	1.0

[a] At 25°, extrapolated from other temperatures when needed. [b] Relative to $Cr(H_2O)_5Br^{2+}$; the value given is $K_X k_X / K_{Br} k_{Br}$. [c] Based on K_a[40] and K_w. [d] Based on equilibrium data in ref 31b and on $K_a(HF) = 1.2 \times 10^{-3}$ M. [e] Estimated from data on $FeN_3{}^{2+}$[46] and $VN_3{}^{2+}$.[47] [f] Reference 40. [g] References 48 and 49. [h] Reference 50.

The mean value[54] of the ratio $k_{\mathrm{YbCo}}/k_{\mathrm{EuCo}}$ was taken as 10^6 resulting in the value of 0.7 for the ratio of electron-exchange rate constants, $k_{\mathrm{Yb}}/k_{\mathrm{Eu}}$. A more complete computation can be made with the inclusion of the value of f.[54-56] This result leads to the revised estimate $k_{\mathrm{Yb}}/k_{\mathrm{Eu}} \approx 70$. Meier and Garner[56a] found that electron exchange between Eu^{3+} and Eu^{2+} occurs immeasurably slowly; Adin and Sykes[11a] suggested an upper limit, $k_{\mathrm{Eu}} < 10^{-5}$ M^{-1} sec^{-1}. Consequently, Adamson's decision not to attempt to measure the rate of Yb^{3+}-Yb^{2+} electron exchange[13] seems correct considering the decomposition rate of Yb^{2+} solutions.

Registry No. $Co(en)_3{}^{3+}$, 14878-41-2; $Co(NH_3)_6{}^{3+}$, 14695-95-5; $Co(NH_3)_5OH_2{}^{3+}$, 14403-82-8; $Cr(NH_3)_5OH_2{}^{3+}$, 15975-47-0; $Cr(NH_3)_5F^{2+}$, 19443-25-5; $Cr(NH_3)_5Cl^{2+}$, 14482-76-9; $Cr(NH_3)_5Br^{2+}$, 22289-65-2; $Cr(H_2O)_5F^{2+}$, 19559-07-0; $Cr(H_2O)_5Cl^{2+}$, 14404-08-1; $Cr(H_2O)_5Br^{2+}$, 26025-60-5; $Cr(H_2O)_5N_3{}^{2+}$, 18517-09-4; $Cr(H_2O)_5NCS^{2+}$, 22258-89-5; $Cr(H_2O)_6{}^{3+}$, 14873-01-9; $Cr(H_2O)_5OH^{2+}$, 27454-20-2; ytterbium, 7440-64-4.

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(53) This area has recently been reviewed: R. G. Linck in "Transition Metals in Homogeneous Catalysis," G. N. Schrauzer, Ed., Marcel Dekker, New York, N. Y., 1971, pp 310-380; see also R. C. Patel and J. F. Endicott, *J. Amer. Chem. Soc.*, 90, 6364 (1968).

(54) The values of k_{YbCo} are from the present work; those for Eu^{2+} for the first two complexes are taken from ref 38 and for $Co(en)_3{}^{3+}$ from ref 7a.

(55) Values of f can be estimated using published data on the Eu^{3+}-Eu^{2+} exchange rate ($<10^{-5}$ M^{-1} sec^{-1}),[56a] on the $Co(NH_3)_6{}^{3+}$-$Co(NH_3)_6{}^{2+}$ exchange rate ($<10^{-9}$ M^{-1} sec^{-1}),[56b] and on the reduction potential for $Co(NH_3)_6{}^{3+}$ (0.1 V). Using the limits as the applicable values where necessary, $f_{\mathrm{EuCo}} = 0.55$ and $f_{\mathrm{YbCo}} = 0.005$.

(56) (a) D. J. Meier and C. S. Garner, *J. Phys. Chem.*, 56, 583 (1952); (b) N. S. Birader, D. R. Stranks, and M. S. Vaidyga, *Trans. Faraday Soc.*, 58, 2421 (1962).