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Assignment of Mechanism to Titanium(III) Reductions of Cobalt(III) Complexes. Hard and Soft Theory as a Means of Assessing Bridging Ligands for Inner-Sphere Electron Transfer

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Received September 9, 1975 AIC506654

The hexaaquotitanium(III) reductions of the cobalt(III) complexes $Co(NH_3)_5X^{(3-n)+}$, with $X^{n-} = F^-, Cl^-, Br^-, I^-, SO_4^{2-}$, NH_3, H_2O, and DMN (*N,N*-dimethylnicotinamide), $Co(bpy)_3^{3+}$, and the μ-superoxo complex $(NH_3)_5CoO_2Co(NH_3)_5^{5+}$ have been studied at 25 °C, $I = 0.5$ M (LiCl). The dependence of second-order rate constants, k_{obsd}, on $[H^+]$ has been investigated over the range 0.05–0.44 M and is of the general form $k_{obsd} = k_0 + k_1[H^+]^{-1}$, where k_1 is effective in all cases, but k_0 is detected only for $Co(NH_3)_5I^{2+}$ and the μ-superoxo complex. For the complex $X^{n-} = F^-$ the $[H^+]$ dependence takes the form $1/k_{obsd} = a + b[H^+]$, where the magnitude of the parameters a and b is indicative of precursor complex formation. From a comparison of rate constants with those for $Ru(NH_3)_6^{2+}$ and V^{2+} reductions of the same complexes (log–log plots), it is concluded that the Ti(III) reductions of $Co(NH_3)_5SO_4^+$, $Co(NH_3)_5(O_2CCH_3)^{2+}$, and the μ-superoxo complex are also inner sphere and that other reactions studied are outer sphere. Potential bridging ligands in these and other reactions can be assessed in terms of the hard and soft acid–base concept.

Recently Martin and Gould[1] have investigated the Ti(III) reduction of carboxylatopentaamminecobalt(III) complexes and from the rate constant pattern concluded that carboxylate functions as a bridging ligand for inner-sphere electron transfer. From the $[H^+]$ dependence Birk[2] has obtained evidence for precursor complex formation (and therefore an inner-sphere mechanism) in the Ti(III) reduction of $Co(NH_3)_5N_3^{2+}$. Information on the Ti(III) reductions of $Co(NH_3)_5Cl^{2+}$, and *cis*- and *trans*-$Co(en)_2Cl_2^+$ has been obtained by Orhanovic and Earley,[3] but inner- or outer-sphere assignments remain in some doubt. At the same time we have been studying the Ti(III) reduction of other $Co(NH_3)_5X^{(3-n)+}$ complexes, $Co(bpy)_3^{3+}$ and $(NH_3)_5CoO_2Co(NH_3)_5^{5+}$, with a view to assigning inner- or outer-sphere mechanisms. The Ti(III) reductions of vanadium(IV) and -(V)[4,5] have previously been reported from these laboratories. Other Ti(III) redox studies have also been reported.[6-8]

Experimental Section

Titanium(III) Solutions. Titanium metal sponge (Johnson and Matthey Chemicals Ltd., 0.5 g) was dissolved in concentrated hydrochloric acid (10 ml) maintained at 40–50 °C (ca. 6 h) in air-free conditions. Excess solid was removed using a porosity No. 4 filter, and the solution was diluted sixfold with N_2-degassed water. The Ti(III) was standardized by addition of an excess of Ce(IV) and back-titrating with Fe(II) in 1 M H_2SO_4 using ferroin as indicator. The absorption coefficient, ϵ 3.97 M^{-1} cm^{-1} at 502 nm, was used for subsequent standardizations. The hydrogen ion concentration was determined by passing aliquot portions down a column of Amberlite IR 120(H) cation-exchange resin. The $[H^+]$ of the eluent solution was determined by titration with 0.1 M NaOH. Stock solutions had $[Ti(III)] = 0.08$–0.17 M and $[H^+] = 0.4$–1.0 M, with $[Ti(IV)] \leq 1\%$ of the [Ti(III)]. Solutions were stored in air-free conditions at 0 °C for up to 2 weeks.

Cobalt(III) Complexes. The complexes $Co(NH_3)_5F^{2+}$,[9] $Co(NH_3)_5Cl^{2+}$,[10] $Co(NH_3)_5Br^{2+}$,[11] $Co(NH_3)_5I^{2+}$,[12] $Co(NH_3)_5SO_4^+$,[13] $Co(NH_3)_5H_2O^{3+}$,[14] $Co(NH_3)_6^{3+}$,[15] $Co(bpy)_3^{3+}$,[16] and $(NH_3)_5CoO_2Co(NH_3)_5^{5+}$ [17] were prepared as chloride salts, and $Co(NH_3)_5(DMN)^{3+}$ was prepared as the perchlorate salt.[18] Uv–visible spectra were in good agreement with existing literature values, Table I.

Table I. Details of Uv–Visible Spectra of Cobalt(III) Complexes (from Ref 19 Except As Stated)

Complex	λ_{max}, nm	ϵ, M^{-1} cm^{-1}	λ_{max}, nm	ϵ, M^{-1} cm^{-1}
$Co(NH_3)_5F^{2+}$	352[a]	38	511	45
$Co(NH_3)_5Cl^{2+}$	362[a]	45	530	47.3
$Co(NH_3)_5Br^{2+}$			551[a]	53
$Co(NH_3)_5I^{2+}$	388	2700	580[a]	79
$Co(NH_3)_5H_2O^{3+}$	345[a]	44	492	47
$Co(NH_3)_5SO_4^{+}$ [b]	357[a]	34.8	517	65.5
$Co(NH_3)_5(DMN)^{3+}$ [c]	334[a]	86.5	475	63.2
$Co(NH_3)_6^{3+}$	339[a]	47	473[a]	58
$Co(bpy)_3^{3+}$ [d]			448[e]	67.9
$[(NH_3)_5Co]_2O_2^{5+}$ [f]	297[a]	2.45×10^4	670[a]	890

[a] Wavelength used for kinetic studies. [b] Reference 13. [c] Reference 18. [d] Reference 24. [e] Kinetics followed at 420 nm (ϵ 57.1 M^{-1} cm^{-1}). [f] See, e.g., A. G. Sykes and J. A. Weil, *Prog. Inorg. Chem.*, **13**, 36 (1970).

Other Reagents. Solutions of chromium(II) perchlorate, $LiClO_4$, and $HClO_4$ were prepared as described previously.[20] Lithium chloride (Hopkin and Williams Reagent grade) was recrystallized twice. The hydrochloric acid was Analar grade reagent.

Rate Measurements. All reactions conform to the stoichiometric equation

$$Ti(III) + Co(III) \rightarrow Ti(IV) + Co(II) \quad (1)$$

except with the μ-superoxo complex where the reduction $\mu(O_2^-) \rightarrow \mu(O_2^{2-})$ occurs. Reactions were monitored by following absorbance (A) changes at peak positions of the oxidant, Table I. The Ti(III) reactant was in large (generally >10-fold) excess. Plots of log ($A_t - A_\infty$) against time were linear to >80% reaction for all but Co-

Table II. Rate Constants, k_{obsd}, for the Ti(III) Reduction of $Co(NH_3)_5Cl^{2+}$ at 25 °C, $I = 0.5$ M (LiCl)

$[H^+]$, M	10^2-$[Ti^{III}]$, M	10^3-$[Co^{III}]$, M	$[ClO_4^-]$, M	10^3k_{obsd}, $M^{-1}\ s^{-1}$
0.050	0.56	0.45		38.0
0.073	2.48	1.82		24.8
0.106	3.72	1.82		15.4
0.139	1.30	0.91		13.3
0.143	1.30	0.91	0.28	12.8
0.160	1.30	0.91		11.2
0.160	1.30	0.91	0.23	11.3
0.170	1.30	0.91	0.28	8.6
0.196	1.30	0.91		10.1
0.250	1.30	0.91		8.3

Table III. Rate Constants, k_{obsd}, for the Ti(III) Reduction of Cobalt(III) Oxidants at 25 °C, $I = 0.5$ M (LiCl)

$[H^+]$, M	10^2-$[Ti^{III}]$, M	10^3-$[Co^{III}]$, M	10^3k_{obsd}, $M^{-1}\ s^{-1}$
	$Co(NH_3)_5Br^{2+}$ Oxidant		
0.066	0.53	0.50	21.0
0.070	2.14	0.60	17.4
0.071	1.07	0.50	18.7
0.105	1.84	0.50	11.5
0.111	1.13	0.50	13.0
0.143	1.13	0.50	9.1
0.180	5.30	0.50	6.0
0.437	1.00	0.30	4.0
	$Co(NH_3)_5I^{2+}$ Oxidant		
0.055	0.95	1.00	89
0.060	0.59	0.50	86
0.080	1.07	1.40	77
0.083	1.04	0.52	70
0.160	0.53	0.50	65
0.390	2.08	0.52	53
0.437	1.04	1.00	57
0.438	1.04	0.50	54
	$Co(NH_3)_5SO_4^+$ Oxidant		
0.060	1.24	1.42	314
0.076	1.24	1.42	272
0.120	2.45	1.90	157
0.221	2.45	2.0	81.2
0.287	2.45	2.0	58.7
0.357	2.45	1.9	54.6
	$Co(NH_3)_5H_2O^{3+}$ Oxidant		
0.112	1.02	1.04	2.06
0.165	1.63	1.70	1.48
0.190	2.03	2.30	1.18
0.235	2.60	3.00	0.90
0.310	2.03	2.30	0.66
	$Co(NH_3)_6{}^{3+}$ Oxidant		
0.083	1.07	0.50	0.35
0.100	1.05	0.48	0.35
0.140	1.05	0.50	0.17
0.200	1.10	0.50	0.16
0.430	1.07	0.49	0.12
	$Co(NH_3)_5(DMN)^{3+}$ Oxidant		
0.068	2.10	0.67	5.9
0.135	4.16	0.67	3.44
0.170	5.40	1.87	2.70
0.253	4.16	0.67	1.73
	$Co(bpy)_3{}^{3+}$ Oxidant		
0.064	1.22	0.35	680
0.100	1.22	0.35	467
0.200	1.22	0.70	238
0.300	0.17	0.17	150

$(NH_3)_6{}^{3+}$ (>60%, low solubility of complex and slow reaction) and those reactions in which perchlorate was present, when the Ti(III) reduction of perchlorate was also effective.[21] Rate constants were evaluated from slopes (×2.303). For the slower reactions Unicam SP500 and SP8000 spectrophotometers were used, and for the faster runs with $Co(NH_3)_5F^{2+}$ and $(NH_3)_5CoO_2Co(NH_3)_5{}^{5+}$ reactions were monitored on a Durrum–Gibson stopped-flow spectrophotometer. All runs were at 25 °C and except as stated were in chloride media with ionic strength adjusted to $I = 0.5$ M (LiCl). Perchlorate when present was introduced via the oxidant solution.

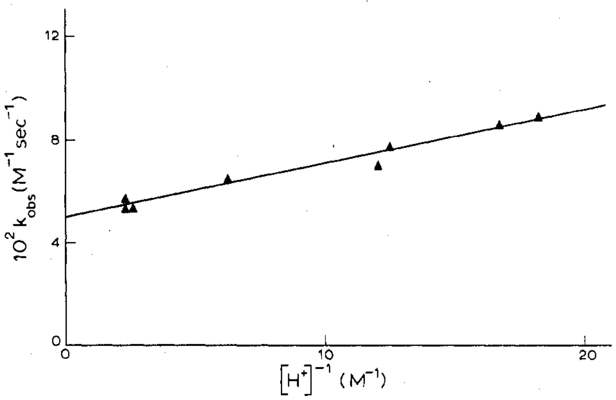

Figure 1.

Table IV. Rate Constants, k_{obsd}, for the Ti(III) Reduction of $Co(NH_3)_5F^{2+}$ at 25 °C, $I = 0.5$ M (LiCl)

$[H^+]$, M	10^2-$[Ti^{III}]$, M	10^3-$[Co^{III}]$, M	10^{-2}-k_{obsd}, $M^{-1}\ s^{-1}$	10^{-2}-k_{calcd},^{a} $M^{-1}\ s^{-1}$
0.050	0.74	0.65	4.18	3.93
0.055	0.74	0.65	3.88	3.85
0.063	0.87	0.85	3.60	3.66
0.065	0.74	0.65	3.72	3.64
0.066	1.73	0.85	3.70	3.64
0.075	0.74	0.65	3.47	3.39
0.079	0.59	0.50	3.00	3.33
0.083	1.73	0.85	3.30	3.27
0.097	2.60	0.85	2.94	3.03
0.100	0.59	0.50	2.78	2.99
0.120	0.59	0.50	2.83	2.74
0.124	2.60	0.85	2.46	2.70
0.130	0.59	0.50	2.60	2.63
0.281	0.87	0.85	1.57	1.61
0.311	1.73	0.85	1.48	1.49
0.342	2.60	0.85	1.35	1.39
0.370	2.05	2.62	1.36	1.31

^{a} From equation 5 and computed values of a and b.

Results

All reactions conform to the rate law

$$\text{rate} = k_{obsd}[Ti(III)][Co(III)] \tag{2}$$

Second-order rate constants k_{obsd} are listed in the tables. Replacement of Cl^- by ClO_4^- had no effect on k_{obsd} for the reduction of $Co(NH_3)_5Cl^{2+}$, Table II, but did give reduced linearity. Dependencies on $[H^+]$ were investigated from 0.05 to 0.44 M, Tables II and III, and conform to

$$k_{obsd} = k_0 + k_1[H^+]^{-1} \tag{3}$$

where k_0 is small and negligible except with $Co(NH_3)_5I^{2+}$ (0.050 ± 0.002 $M^{-1}\ s^{-1}$; see Figure 1) and the μ-superoxo complex (280 ± 90 $M^{-1}\ s^{-1}$). Consistent with an acid dissociation constant K_a = ca. 2×10^{-3} M at 25 °C, as determined by Paris and Gregoire[22] and Krentzien and Brio,[23] no curvature is apparent in plots of k_{obsd} against $[H^+]^{-1}$ over the $[H^+]$ range investigated. For a more precise evaluation of k_1 we have assumed (4) to apply with $K_a = 2 \times 10^{-3}$ M. For

$$k_{obsd} = k_1/(K_a + [H^+]) \tag{4}$$

the range of reactant concentrations chosen with $Co(bpy)_3{}^{3+}$ as oxidant, dissociation of the primary product $Co(bpy)_3{}^{2+}$ is rapid[24] compared to the redox step. Rate constants for the reaction of $Co(NH_3)_5F^{2+}$, Table IV, give a fit to (5), which

$$1/k_{obsd} = a + b[H^+] \tag{5}$$

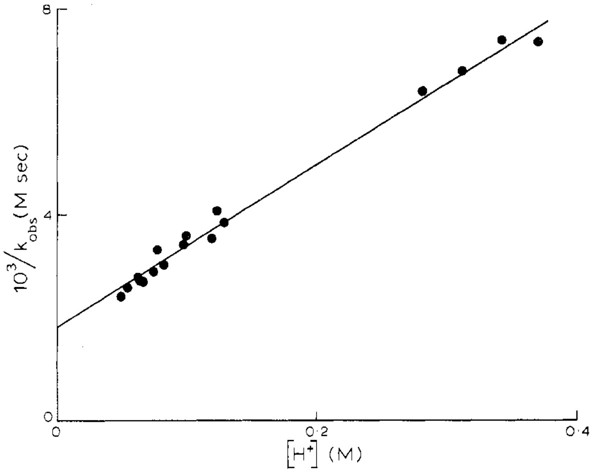

Figure 2.

is of the same form as (4) but requires $K_a >> 2 \times 10^{-3}$ M. A graph of $1/k_{obsd}$ against [H$^+$] gives $a = (1.78 \pm 0.08) \times 10^{-3}$ M s and $b = (15.9 \pm 0.4) \times 10^{-3}$ s (see Figure 2).

The Ti(III) reduction of the μ-superoxo complex was monitored at 670 nm (one stage) and at 297 nm (two stages). Using standard consecutive reaction treatment[25] rate constants k_1 and k_2 were evaluated for the two stages at 297 nm. The constant k_1 is in excellent agreement with values obtained at 670 nm, Table V, and corresponds to the redox step involving reduction of the μ-superoxo complex. The second k_2 corresponds to the μ-peroxo decomposition which may be written as in (6). Rate constants k_2 exhibit an inverse dependence

$$(NH_3)_5CoO_2Co(NH_3)_5{}^{4+} \xrightarrow{H^+} 2Co(II) + O_2 + 10NH_4{}^+ \qquad (6)$$

on [H$^+$] as reported by Hoffman and Taube[26] but are less than those reported in the latter work. However further experiments have shown that k_2 but not k_1 is dependent on [Cl$^-$], being slowest when an exclusively chloride medium is used. If the first step is inner sphere, then it is possible that the μ-peroxo complex will have Ti(IV) attached. To test whether k_2 is the same as is observed in the Cr^{2+} reduction of the μ-superoxo complex a number of runs were performed with Cr^{2+} as reductant in the presence of chloride. Rate constants obtained at 25 °C, $I = 1.0$ M, with [H$^+$] = 0.84 M and [Cl$^-$] = 0.50 M, were 1.99 s^{-1} with Ti(III) and 2.20 s^{-1} with Cr^{2+}. The close agreement suggests that an appended Ti(IV) has little effect on (6) or that the same μ-peroxo species is present in both cases.

Discussion

Details of the Ti(III) reduction of perchlorate have been reported previously.[21] To avoid complications arising from this reaction it was decided to use chloride reactant solutions in this study. As in the Ti(III) reduction of V(V)[5] we find that rate constants for the reduction of $Co(NH_3)_5Cl^{2+}$ (Table II) and $(NH_3)_5CoO_2Co(NH_3)_5{}^{5+}$ (Table V) are unaffected by the replacement of free chloride by perchlorate, $I = 0.5$ M (LiCl). It has also been demonstrated that the replacement of chloride by trifluoromethylsulfonate gives identical rate constants.[3] Values of k_1 which we give for $Co(NH_3)_5(DMN)^{3+}$ are consistent with the estimate $<6 \times 10^{-4}$ M^{-1} s^{-1} in *p*-toluenesulfonic acid.[1]

Table V. Rate Constants, k_{obsd}, for the Ti(III) Reduction of $(NH_3)_5CoO_2Co(NH_3)_5{}^{5+}$ at 25 °C, $I = 0.5$ M (LiCl), and λ 670 nm, Except As Stated. The Second Stage (k_2) Corresponds to the Decomposition of the μ-Peroxo Product

[H$^+$], M	10^2-[Ti^{III}], M	10^5[μ-(O_2^-)], M	$10^{-3}k_{obsd}$, M^{-1} s^{-1}	k_2, s^{-1}
0.055	0.89	2.80	3.6	
0.056	0.82	12.3	3.56	
0.081	3.35	3.9	2.3	
0.082	3.35	1.09	2.3[a]	13.3[a]
0.086	0.40	3.9	3.0	
0.086	0.40	1.09	2.45[a]	
0.100	0.089	2.80	2.2	
0.113	3.35	2.18	2.26[a]	11.5[a]
0.113	3.35	7.9	1.85	
0.118	0.40	7.9	2.00	
0.118	0.40	2.18	1.86[a]	
0.175	3.35	0.50	1.13[a]	7.05[a]
0.175	3.35	15.9	1.22	
0.180	0.40	15.9	1.39	
0.200	0.82	12.3	1.32	
0.240	3.35	0.25	0.93[a]	4.56[a]
0.305	0.40	31.9	0.81	
0.300	3.35	31.9	0.78	
0.310	0.82	2.8	1.01	
0.45	0.82	2.8	0.72	
0.80[b,c]	3.35	1.6	0.36[a]	0.88[a]
0.80[b,d]	3.35	1.6	0.36[a]	2.82[a]
0.82[b,e]	6.8	1.6		1.21[a]
0.82[b,d]	6.8	1.6		1.99[a]

[a] λ 297 nm. [b] $I = 1.0$ M (LiCl). [c] [ClO_4^-] = 0.05 M. [d] [ClO_4^-] = 0.55 M. [e] [ClO_4^-] = 0.25 M.

The [H$^+$] dependence of all but the $Co(NH_3)_5F^{2+}$ reaction may be discussed in terms of (3). We are unable to offer an explanation for the relatively large contribution of k_0 with $Co(NH_3)_5I^{2+}$ as oxidant, Figure 1. An intercept corresponding to k_0 was also obtained with the μ-superoxo complex but was not detected in other cases. Contributions from k_0 have also been observed in the Ti(III) reductions of *cis*- and *trans*-$Co(en)_2Cl_2{}^+$.[3] Values of k_1 were obtained from (4) assuming $K_a = 2 \times 10^{-3}$ M. Martin and Gould[1] reported a good fit to their data with $K_a = 1.6 \times 10^{-3}$ M; Orhanovic and Earley,[3] on the other hand, have deduced a somewhat higher value of $K_a = 4.6 \times 10^{-3}$ M from their kinetic data. The path k_1 is presumably favored because of the increase in degree of hydrolysis involved in the oxidation to TiO^{2+}. True rate constants for the reaction of $TiOH^{2+}$ are given by k_1/K_a. A possible ambiguity arises in the case of $Co(NH_3)_5H_2O^{3+}$ since Ti^{3+} reduction of $Co(NH_3)_5OH^{2+}$ may contribute. However the acid dissociation constant for $Co(NH_3)_5H_2O^{3+}$ is much smaller ($10^{-6.3}$ M),[27] and since the data conform to the correlations cited below, major contributions from this path seem unlikely.

Earlier studies on redox[28,29] and substitution[30] reactions of $Co(NH_3)_5F^{2+}$ have given no indication of extensive protonation of F$^-$. We are not aware of any previous measurement of a protonation constant for $Co(NH_3)_5F^{2+}$, and in separate experiments we were unable to detect any spectrophotometric changes in the region 230–600 nm with varying concentrations of perchloric acid, [H$^+$] = 0.1–2.0 M, $I = 2.0$ M ($LiClO_4$). There are no grounds for supposing therefore that in the Ti(III) reduction of $Co(NH_3)_5F^{2+}$ the acid dissociation of $Co(NH_3)_5FH^{3+}$ is relevant in (5). Likewise acid dissociation of the Ti(III) reactant will not account for the data obtained. Rather is the dependence (5) indicative of a two-stage process involving a precursor complex. One possible reaction sequence which we would favor involves a rapid equilibration (7) followed by the electron-transfer step (8). Making the sta-

$$Ti(H_2O)_6{}^{3+} + Co(NH_3)_5F^{2+} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} [(HO)(H_2O)_4TiFCo(NH_3)_5]^{4+} + H^+ \qquad (7)$$

$$[(HO)(H_2O)_4TiFCo(NH_3)_5]^{4+} \xrightarrow[H^+,\ H_2O]{k_4} TiO^{2+} + Co^{2+} + 5NH_4{}^+ + HF \qquad (8)$$

tionary-state approximation for the binuclear species expression 9 is obtained which is of the same form as (5). The

Table VI. Summary of Rate Constants for the Ti(III), $Ru(NH_3)_6^{2+}$, and V^{2+} Reductions of Cobalt(III) Oxidants[o]

	Oxidant	k_1, s^{-1}	k_{Ru}, M^{-1} s^{-1}	k_V, M^{-1} s^{-1}
A	$Co(NH_3)_5(O_2CCH_3)^{2+}$	4.9×10^{-3} [a]	0.022[c]	1.15[g]
B	$Co(NH_3)_5SO_4^+$	1.98×10^{-2}	12.9[d]	25.5[h]
C	$Co(NH_3)_5H_2O^{3+}$	2.49×10^{-4}	3.0[e]	0.53[i]
D	$Co(NH_3)_6^{3+}$	3.0×10^{-5}	0.024[c]	3.7×10^{-3} [i]
E	$Co(NH_3)_5(DMN)^{3+}$	4.2×10^{-4}	3.7[c]	1.38[j]
F	$Co(NH_3)_5Cl^{2+}$	1.89×10^{-3}	2.6×10^2 [e]	10.2[k]
G	*cis*-$Co(en)_2Cl_2^+$	3.5×10^{-3} [b]	8.8×10^2 [e]	24.0[l]
H	$Co(NH_3)_5Br^{2+}$	1.3×10^{-3}	1.6×10^3 [e]	30.0[k]
I	$Co(NH_3)_5 I^{2+}$	2.11×10^{-3}	6.7×10^3 [e]	127[k]
J	*trans*-$Co(en)_2Cl_2^+$	1.45×10^{-2} [b]	9.0×10^3 [e]	128[l]
K	$Co(bpy)_3^{3+}$	4.4×10^{-2}	6.9×10^5 [d]	1.1×10^3 [m]
L	$(NH_3)_5CoO_2Co(NH_3)_5^{5+}$	1.86×10^2	3.7×10^6 [f]	9.4×10^4 [n]

[a] Reference 1. [b] Reference 3. [c] Reference 43. [d] Reference 32. [e] J. F. Endicott and H. Taube, *J. Am. Chem. Soc.*, **86**, 1686 (1964). [f] Reference 33. [g] M. Barrett, J. H. Swinehart, and H. Taube, *Inorg. Chem.*, **10**, 1983 (1971). [h] M. Green, R. S. Taylor, and A. G. Sykes, *J. Chem. Soc. A*, 509 (1971). [i] A. Zwickel and H. Taube, *J. Am. Chem. Soc.*, **83**, 793 (1961). [j] Reference 42. [k] Reference 29. [l] Reference 35. [m] Reference 24. [n] Reference 26. [o] Rate constants k_1, which incorporate K_a, correspond to the reactions of $TiOH^{2+}$.

$$k_{obsd} = k_4k_3/(k_{-3}[H^+] + k_4) \qquad (9)$$

constants *a* and *b* in (5) give $k_3 = 56.2$ M^{-1} s^{-1} and $k_4/k_{-3} = 0.112$ M. Other reaction sequences giving rise to the same $[H^+]$ dependence are possible. Birk[2] has observed identical behavior in the Ti(III) reduction of $Co(NH_3)_5N_3^{2+}$. The values of k_3 and k_4/k_{-3} compare with values 47 M^{-1} s^{-1} and 0.045 M obtained by Birk. Bearing in mind the unfavorable charge product of the reactant, the values obtained for k_3 are certainly consistent with a Ti(III) substitution-controlled process.[31]

To enable a comparison of rate constants to be made with $Ru(NH_3)_6^{2+}$ as reductant (k_{Ru}), Table VI, independent studies of the $Ru(NH_3)_6^{2+}$ reductions of $Co(NH_3)_5SO_4^+$ and $Co(bpy)_3^{3+}$ were made, $[H^+] = 10^{-3}$ M, $I = 0.1$ M ($LiClO_4$).[32] These have yielded rate constants (25 °C) of 12.9 and 6.9×10^5 M^{-1} s^{-1}, respectively, which are assumed to be independent of $[H^+]$. For outer-sphere reactions a plot of log k_{Ru} against log k_1 should give a linear correlation and provides a powerful means of identifying this mechanism. The Ti(III) reductions of $Co(NH_3)_6^{3+}$, $Co(NH_3)_5(DMN)^{3+}$, and $Co(bpy)_3^{3+}$ must be outer sphere (since there are no available sites for inner-sphere reduction), and points lying on or near to the line defined by these points, Figure 3, can be assigned an outer-sphere mechanism. Rate constants k_1 for *cis*- and *trans*-$Co(en)_2Cl_2^+$ [3] and $Co(NH_3)_5(O_2CCH_3)^{2+}$ [1] are as determined in other studies, $I = 1.0$ M. Equation 10

$$\log k_1 = (0.40 \pm 0.04) \log k_{Ru} - (3.79 \pm 0.14) \qquad (10)$$

summarizes the correspondence of the nine data points C–K to this line (unweighted least squares). Conversely the points for $Co(NH_3)_5(O_2CCH_3)^{2+}$ (A), $Co(NH_3)_5SO_4^+$ (B), and the μ-superoxo complex (L) lie away from this line and must on this evidence involve inner-sphere reduction by $TiOH^{2+}$, with activated complexes, e.g., $[HO(H_2O)_4TiSO_4Co(NH_3)_5]^{3+}$.

We have also plotted log k_1 values against log k_V for the V^{2+} reduction of the same oxidants, Table VI, Figure 4. Identical inner- and outer-sphere assignments result. The V^{2+} reductions of $Co(NH_3)_5(O_2CCH_3)^{2+}$ and $Co(NH_3)_5SO_4^+$ are believed to be inner-sphere and for this reason do not conform to the line (11). However from the position of these two points above the line it can be concluded that the Ti(III) rate constants also correspond to inner-sphere reactions.

$$\log k_1 = (0.55 \pm 0.06) \log k_V - (3.35 \pm 0.11) \qquad (11)$$

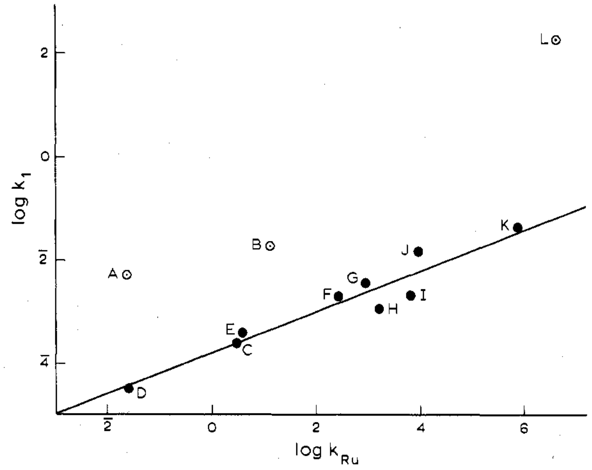

Figure 3.

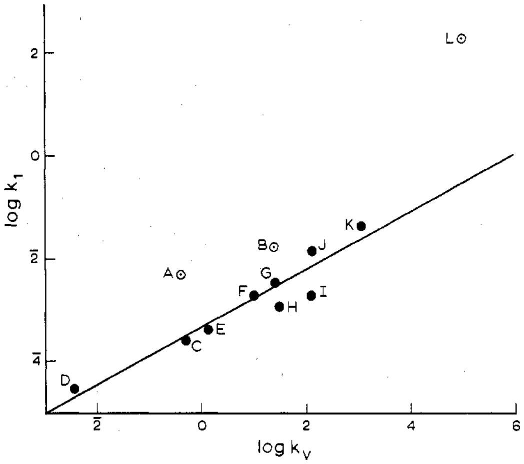

Figure 4.

The assignment for the Ti(III) reduction of the μ-superoxo complex requires further comment, since the Cr^{2+}, V^{2+}, and Eu^{2+} reductions of this complex[26] are all outer sphere on the basis of log–log correlations.[33] This is the first time that any clear indication has been obtained for the inner-sphere reduction of the μ-superoxo group. As a consequence the Ti(IV) will be bound to the μ-peroxo group in the primary product. Present indications are that Ti(IV) is probably very labile and unless it has a very marked affinity for the μ-peroxo group will rapidly aquate. Certainly Ti(IV) is known to have some affinity for an O_2 group.[34] On addition of Ti(IV) to the μ-superoxo complex no evidence for adduct formation was obtained. We were unable to test for Ti(IV) association with the μ-peroxo complex in view of the instability of the latter. Since the rate of decomposition of the μ-peroxo complex is within experimental error the same whether it is generated by Ti(III) or Cr^{2+} reduction of the μ-superoxo complex, we conclude that the Ti(IV) rapidly dissociates from the primary product and that (6) is then observed.

As a result of this study it can be concluded that the Ti(III) reduction of $Co(NH_3)_5Cl^{2+}$, $Co(NH_3)_5Br^{2+}$, $Co(NH_3)_5I^{2+}$, and *cis*- and *trans*-$Co(en)_2Cl_2^+$ are outer-sphere, whereas the reduction of $Co(NH_3)_5X^{(3-n)+}$ complexes with the harder ligands including SO_4^{2-}, $CH_3CO_2^-$, F^-, and the μ-superoxo complex are inner sphere. Previously it has been demonstrated that the V^{2+} reductions of $Co(NH_3)_5Cl^{2+}$, $Co(NH_3)_5Br^{2+}$, $Co(NH_3)_5I^{2+}$, and *cis*- and *trans*-$Co(en)_2Cl_2^+$ are outer sphere,[29,35] whereas those with $Co(NH_3)_5SO_4^+$, $Co(NH_3)_5(O_2CCH)_3)^{2+}$, and $Co(NH_3)_5F^{2+}$ as well as Co-

$(NH_3)_5N_3^{2+}$ are inner sphere.[36] From water-exchange studies the Ti(III)[31] and (in some cases V^{2+})[37] ions are sufficiently labile for inner-sphere reactions to be observed. Since Ti(III) and V^{2+} are to be regarded as hard ions, clearly the potential of a ligand to function as a bridge can be assessed in terms of hard–soft acid–base theory.[38] We note also that $Co(CN)_5^{3-}$, a soft reductant, reacts with $Co(NH_3)_5F^{2+}$ by both inner- and outer-sphere paths, but with $Co(NH_3)_5Cl^{2+}$ only the inner-sphere path is detected. Clearly assignments for Cl^-, Br^-, and I^- as opposed to F^-, SO_4^{2-}, $CH_3CO_2^-$, and N_3^- are not simply a function of basicity of the ligand since with Cr^{2+} at least all the reactions are of the inner-sphere type.[40]

It has recently become apparent that log–log correlations involving Cr^{2+}, V^{2+}, Eu^{2+} $Ru(NH_3)_6^{2+}$,[41–43] and possibly also $Cr(bpy)_3^{2+}$ [44] as reductant all give slopes close to 1.0.[41–43] The only exception is for the correlation involving the V^{2+} and Fe^{2+} reductions of chlorocobalt(III) complexes, which gives a gradient of 0.49.[35] However the Fe^{2+} reactions are known to be inner sphere, and the existence of a correlation of this type is dependent on all reactions having a common chloride bridging ligand. The slopes in the present cases involving $TiOH^{2+}$ as a reductant are 0.55 and 0.40, respectively. Whether these much lower slopes stem in some way from the orientation of the OH^- attached to the Ti(III) or some concomitant movement of the proton of the OH^- as the electron is transferred (or some other reason) is not at present clear. The scatter in Figures 3 and 4, particularly in the region of the points for $Co(NH_3)_5Br^{2+}$ and $Co(NH_3)_5I^{2+}$, is greater than is generally observed for such plots.

Finally we must concur with Orhanovic and Earley[3] that rate constants reported by Cope et al.[45] appear to be several orders of magnitude in error. Our estimate of the magnitude of K_a is consistent with that of Martin and Gould (see also ref 5). We have avoided working at $[H^+] < 0.05$ M in view of other possible complications which are generally present when hexaaquo ions are involved as reactants. As in the work of Birk we do not find Cl^- inhibition to be effective for runs carried out in perchlorate media, $I = 0.5$ M.

Acknowledgment. We thank Tioxide International and the Science Research Council (London) for financial support. Discussions with Dr. P. Howard of Tioxide International are gratefully acknowledged.

Registry No. $Co(NH_3)_5Cl^{2+}$, 14970-14-0; $Co(NH_3)_5Br^{2+}$, 14970-15-1; $Co(NH_3)_5I^{2+}$, 15392-08-2; $Co(NH_3)_5SO_4^+$, 18661-07-9; $Co(NH_3)_5H_2O^{3+}$, 14403-82-8; $Co(NH_3)_6^{3+}$, 14695-95-5; $Co(NH_3)_5(DMN)^{3+}$, 31011-70-8; $Co(bpy)_3^{3+}$, 19052-39-2; $Co(NH_3)_5F^{2+}$, 15392-06-0; $(NH_3)_5CoO_2Co(NH_3)_5^{5+}$, 12259-09-5; $Ti(H_2O)_6^{3+}$, 17524-20-8.

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