ponent of the reaction leading to the desired end product) using $BaCl_2$ (Allied Chemical) andMn O_2 (Baker Analyzed). $BaCl_2$ (300 g) was charged into a 250-ml Pt dish and was molten at 1000°. MnO_2 (10 g) was charged into the melt and moist air was bubbled through the melt by way of a 0.5-in. diameter platinum tube, perforated at the bottom. The melt was held at 1000° for 2 hr and at 1200° for 1 hr. After furnace cooling excess halide was leached away with water and the product was filtered, washed, and dried. About half of the reaction product was obtained as intensely colored blue-green crystals of acicular habit; the other half (readily separated by flotation) was Mn_3O_4. Chemical analysis of the manganate gave the following results. *Anal.* Calcd for $Ba_5(MnO_4)_3Cl$: Ba, 63.65; Mn, 15.27; Cl, 3.28. Found: Ba, 64.0; Mn, 15.3; Cl, 3.4. The compound was structurally identified as an apatite and X-ray parameters were found to be a_h = 10.38 Å, c_h = 7.73 Å.

Results and Discussion

The observed susceptibility for $Ba_5(MnO_4)_3Cl$ was independent of field from 2000 to 8000 Oe at room temperature, 300°K ($10^3\chi_m = 8.82 \pm 0.08$) and at liquid temperature, 77°K ($10^3\chi_m = 29.6 \pm 0.2$).

After correcting the observed susceptibility for temperature-independent diamagnetism, $10^3\chi_m{}^d = -0.348$, estimated from Pascal's constants, the reciprocal paramagnetic susceptibility $[1/(10^3\chi_m + 0.348)]$ is not quite linear with absolute temperature. The effective moment per manganese at 300°K is 2.69 BM and at 77°K is 2.50 BM.

If a small temperature-independent paramagnetic component of about $+0.497 \times 10^{-3}$ per manganese is included in addition to the diamagnetic correction, the corrected susceptibility follows a Curie–Weiss law with a very small Weiss constant. On a per manganese basis, this is

$$\chi_m - (0.381 \times 10^{-3}) = \frac{0.758 \pm 0.001}{T + (0.34 \pm 0.26)}$$

The magnetic moment calculated from the slope of the Curie–Weiss type of susceptibility is 2.46 BM.

For pentavalent tetrahedral manganese, d^2 (^3A), the expected moment is

$$\mu = 2.83\left(1 - \frac{4\lambda}{10Dq}\right) \simeq 2.6 \text{ BM}$$

essentially independent of temperature.

Hexavalent tetrahedral manganese, d^1 (^2E), should exhibit also an essentially temperature-independent moment

$$\mu = 1.73\left(1 - \frac{2\lambda}{10Dq}\right) \simeq 1.6 \text{ BM}$$

whereas quadrivalent tetrahedral manganese, d^3 ($^4T_1$), should exhibit a significantly temperature-dependent moment, estimated to be about μ = 3.5 BM at 300°K and μ = 2.5 BM at 100°K. Thus, on the basis of an equal mixture of Mn^{4+} and Mn^{6+}, the average moment

$$\bar{\mu} = \sqrt{\frac{\mu_1{}^2 + \mu_2{}^2}{2}}$$

to be observed would be about μ = 2.72 BM at 300°K and 2.10 BM at 100°K.

These observed and calculated magnetic moments are summarized in Table I.

TABLE I

MAGNETIC MOMENTS OF TETRAHEDRAL MANGANESE (IN BM)

Temp, °K	Calcd		Obsd	
	Mn^{5+}	$Mn^{4+}:Mn^{6+}$	μ_{eff}	μ_{slope}
300	~2.6 ± 0.15	~2.7 ± 0.2	2.69	2.46
100	~2.6 ± 0.15	~2.1 ± 0.2		2.46
77	~2.6 ± 0.15	<2.1	2.50	2.46

On the basis of the results presented in Table I, it would seem correct to state that the manganese in $Ba_5(MnO_4)_3Cl$ is indeed in the pentavalent state. Klemm[6] prepared the equivalent hydroxy manganate(V), $Ba_5(MnO_4)_3(OH)$, and observed that this compound is more distinctly blue-green than the regular manganate(V), $Ba_3(MnO_4)_2$. We noted the same difference for $Ba_5(MnO_4)_3Cl$. As a final piece of supporting evidence, we observed the absorption spectrum of $Ba_5(MnO_4)_3Cl$ to be very similar to that of a solution of $MnO_4{}^{3-}$ in strong alkali. Similar observations have been made by Johnson.[7]

All of this evidence clearly supports the statement that $Ba_5(MnO_4)_3Cl$ is a novel barium chloromanganate(V) crystallizing in the apatite structure.

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Correspondence

Reactivity Patterns in Inner- and Outer-Sphere Reductions of Halogenopentaamminecobalt(III) Complexes[1]

Sir:

The reductions of halogenopentaamminecobalt(III) complexes by various reducing agents have been extensively investigated. For all of the reducing agents studied the rate constants vary monotonically as the halide is changed from fluoride to iodide. The reactivity order has come to be known as "normal" or "inverse" depending on whether the rate increases or decreases with increasing atomic number of the halogen. The normal reactivity order (F < Cl < Br < I) is observed for the inner-sphere reductions by chromium(II)[2] and pentacyanocobaltate(II);[3] for the outer-

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(1) This work was supported by the National Science Foundation under Grant GP-6528.

(2) J. P. Candlin and J. Halpern, *Inorg. Chem.*, **4**, 766 (1965).

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

sphere reductions, by tris(bipyridyl)chromium(II)[4] and hexaammineruthenium(II),[5] as well as for the reductions by vanadium(II)[4,6] which proceed by an unknown mechanism. In contrast, the reductions by europium(II)[4] and iron(II)[6,7] which also proceed by unknown mechanisms obey the inverse order (F > Cl > Br > I).

It was noted[2,4] that the latter reactivity order parallels the order of the thermodynamic stabilities of the europium(III) and iron(III) halide complexes. On this basis, it was suggested[2,4] that the inverse order is determined by the driving force for reaction and, therefore, that the inner-sphere mechanism obtains for the europium(II) and iron(II) reductions. The assumptions involved in correlating the reactivity sequence with the standard free energy change for the reactions have been explicitly stated.[6] In this context, it is noteworthy that the reversal in reactivity in the reactions of chromium(II) and iron(II) with the halogenopentaamminecobalt(III) complexes has been predicted by using the Marcus equation.[8]

It is apparent that trying to understand the reactivity orders described above poses a challenging problem, but so far only some of the factors that need to be taken into consideration have been enumerated.[8-10] Moreover, if we accept, as seems likely, that the iron(II) and europium(II) reductions proceed *via* halide-bridged transition states, then it is clear that the reactivity orders are not useful indirect criteria for distinguishing between inner- and outer-sphere mechanisms.

In the present note we wish to examine the reductions of halogenopentaamminecobalt(III) complexes on the basis of formal calculations of equilibrium constants involving transition states.[11] It must be noted that in performing these calculations, it is assumed that the transmission coefficient κ, in the transition-state theory expression $k = \kappa(RT/Nh)K^{\ddagger}$, is unity. Viewed in this manner, the reactions under consideration fall into three categories: (1) inner-sphere reductions by class a or hard metal ions, (2) outer-sphere reductions, and (3) inner-sphere reductions by class b or soft metal ions.

The equilibrium constant for the reaction of the transition state $[(NH_3)_5CoFCr^{4+}]^{\ddagger}$ with iodide ion to produce the transition state $[(NH_3)_5CoICr^{4+}]^{\ddagger}$ and fluoride ion (eq 5) can be obtained by appropriate combination of reactions 1–4. The value of Q_5 (subject to the validity of the above assumption) gives a measure of the relative stabilities of the transition states with fluoride and iodide bridges, and it is seen that this formal calculation effectively provides a correction of the rate constant ratio k_2/k_1 for the difference in free energies of the ground states.

$$Co(NH_3)_5F^{2+} + Cr^{2+} \rightleftharpoons [(NH_3)_5CoFCr^{4+}]^{\ddagger} \qquad k_1 \quad (1)$$

$$Co(NH_3)_5I^{2+} + Cr^{2+} \rightleftharpoons [(NH_3)_5CoICr^{4+}]^{\ddagger} \qquad k_2 \quad (2)$$

$$Co(NH_3)_5OH_2^{3+} + F^- \rightleftharpoons Co(NH_3)_5F^{2+} + H_2O \qquad Q_3 \quad (3)$$

$$Co(NH_3)_5OH_2^{3+} + I^- \rightleftharpoons Co(NH_3)_5I^{2+} + H_2O \qquad Q_4 \quad (4)$$

$$[(NH_3)_5CoFCr^{4+}] + I^- \rightleftharpoons [(NH_3)_5CoICr^{4+}]^{\ddagger} + F^- \qquad Q_5 = k_2Q_4/k_1Q_3 \quad (5)$$

The results of our calculations are presented in Table I and depicted schematically in Figure 1. Some comments regarding the calculations in Table I are pertinent. For the vanadium(II) reductions, we chose to calculate the equilibrium constant for substitution of fluoride by bromide rather than by iodide. The rate constants for the reductions of $Co(NH_3)_5F^{2+}$, $Co(NH_3)_5Cl^{2+}$, and $Co(NH_3)_5Br^{2+}$ by vanadium(II) fall in the range 5–15 M^{-1} sec^{-1}, characteristic of inner-sphere reductions,[12-14] whereas the rate constant for $Co(NH_3)_5I^{2+}$ is 1.2×10^2 M^{-1} sec^{-1}, a value that suggests the operation, at least in part, of an outer-sphere mechanism.[12] The reductions by iron(II) and europium(II) are formulated as inner-sphere reactions. Direct evidence for bridged transition states in the reduction of a variety of cobalt(III) complexes by iron(II) has been previously presented.[15] The mechanism is unknown for europium(II), but, as will be seen below, the present comparisons suggest an inner-sphere mechanism. When the rate constants for reductions of the fluoro- or iodopentaamminecobalt(III) complexes have not been

TABLE I

FORMAL EQUILIBRIUM CONSTANTS AT 25° FOR SUBSTITUTION OF HALIDE IONS IN VARIOUS TRANSITION STATES[a]

Reaction	Q
$[(NH_3)_5CoFCr^{4+}]^{\ddagger} + I^- \rightleftarrows [(NH_3)_5CoICr^{4+}]^{\ddagger} + F^-$	6.4×10^{-2}
$[(NH_3)_5CoFV^{4+}]^{\ddagger} + Br^- \rightleftarrows [(NH_3)_5CoBrV^{4+}]^{\ddagger} + F^-$	7.3×10^{-2}
$[(NH_3)_5CoFFe^{4+}]^{\ddagger} + Br^- \rightleftarrows [(NH_3)_5CoBrFe^{4+}]^{\ddagger} + F^-$	1.6×10^{-3}
$[(NH_3)_5CoFEu^{4+}]^{\ddagger} + I^- \rightleftarrows [(NH_3)_5CoIEu^{4-}]^{\ddagger} + F^-$	2.2×10^{-5}
$[(NH_3)_5CoClRu(NH_3)_6^{4+}]^{\ddagger} + I^- \rightleftarrows [(NH_3)_5CoIRu(NH_3)_6^{4+}]^{\ddagger} + Cl^-$	2.5×10^{2}
$[(NH_3)_5CoFCr(bipy)_3^{4+}]^{\ddagger} + Br^- \rightleftarrows [(NH_3)_5CoBrCr(bipy)_3^{4+}]^{\ddagger} + F^-$	3.9×10^{2}
$[(NH_3)_5CoFCo(CN)_5^{-}]^{\ddagger} + Br^- \rightleftarrows [(NH_3)_5CoBrCo(CN)_5^{-}]^{\ddagger} + F^-$	$>1.6 \times 10^{4}$

[a] Rate constants used in calculations taken from ref 2–7. Equilibrium constants taken from: D. A. Buckingham, I. I. Olsen, A. M. Sargeson, and H. Satrapa, *Inorg. Chem.*, **6**, 1027 (1967); C. H. Langford, *ibid.*, **4**, 265 (1965). The equilibrium constants at 25° for the formation of $Co(NH_3)_5X^{2+}$ (X = F, Cl, Br, I) from $Co(NH_3)_5OH_2^{3+}$ and the appropriate halide are 25, 1.11, 0.35, and 0.12 M^{-1} for F, Cl, Br, and I, respectively.

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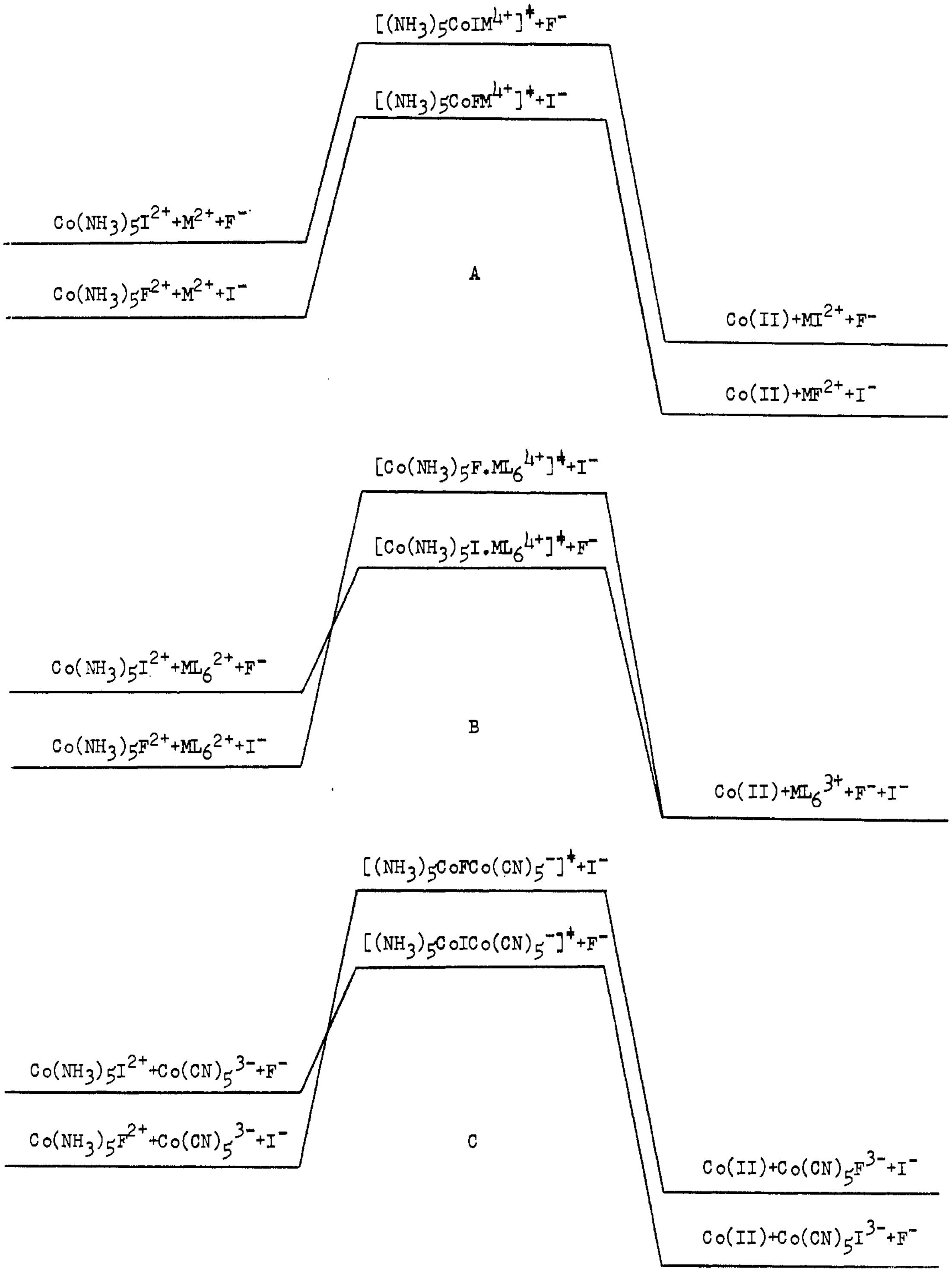

Figure 1.—Schematic free energy diagram of reactants, transition states, and products for three categories of reactions: A, $Co(NH_3)_5X^{2+} + M^{2+}$ (M = Cr, V, Fe, Eu); B, $Co(NH_3)_5X^{2+} + ML_6^{2+}$ ($ML_6 = Ru(NH_3)_6, Cr(bipy)_3$); C, $Co(NH_3)_5X^{2+} + Co(CN)_5^{3-}$.

reported, the calculations are carried out for the corresponding chloride or bromide complexes, respectively. Equilibrium constants involving the intermediate halides are not included in Table I. However, in all cases the equilibrium constants vary monotonically as one goes through the sequence Cl, Br, I.

An examination of the values of Q listed in Table I reveals that, for chromium(II), iron(II), europium(II), and vanadium(II), the substitution of a bridging fluoride by a bridging iodide (or bromide) is an *unfavorable* process. Therefore, using the values of Q as a measure of stability, it is seen that the stability order of the transition states is F > Cl > Br > I and is the same as the reactivity order for iron(II) and europium(II), but opposite to that for chromium(II) and vanadium(II). It is noteworthy that when one compares reactivities, these four reducing agents fall into two classes. However, when one compares the stabilities of the transition states, all of these reducing agents exhibit a common sequence.

For the outer-sphere reductions by $Cr(bipy)_3^{2+}$ and $Ru(NH_3)_6^{2+}$, the substitution of a coordinated fluoride (or chloride) by bromide (or iodide) is a *favorable* process, and, therefore, the stability order of transition states $F < Cl < Br < I$ is the same as the reactivity order. Finally, for the inner-sphere reductant $Co(CN)_5^{3-}$, substitution of fluoride by bromide is favorable, and the stability order for the transition states ($F < Cl < Br < I$) is the same as the reactivity order.

The differences between the three categories are displayed in Figure 1. For the reductions by the class a[16] or hard[17] metal centers, the stability orders for reactants, transition states, and products follow the sequence $F > Cl > Br > I$. For the outer-sphere reactions, there is a reversal in stability order as one goes from reactants ($F > Cl > Br > I$) to transition states ($F < Cl < Br < I$). Finally, for the inner-sphere reductions by the soft[18] center $Co(CN)_5^{3-}$, the stability order of the transition states and the products ($F < Cl < Br < I$) is the reverse of the stability order of the reactants.

Two other notable classes of reactions that follow the normal reactivity order are the chromium(II)-catalyzed dissociation of halogenopentaamminechromium(III) complexes[19] and the exchange of chromium atoms between halogenopentaaquochromium(III) complexes and chromium(II).[20] Unfortunately, no thermodynamic data are available for the pentaammine series. However, equilibrium constants have been reported for the formation of $Cr(H_2O)_5F^{2+}$ and $Cr(H_2O)_5Cl^{2+}$.[21,22] Combining these values with the rate constants for the $Cr(H_2O)_5F^{2+}$–Cr^{2+} and $Cr(H_2O)_5Cl^{2+}$–Cr^{2+} reactions,[20] we arrive at a value of $Q_6 \sim 1.5 \times 10^{-2}$ for

$$[(H_2O)_5CrFCr^{4+}]^{\ddagger} + Cl^- \rightleftharpoons [(H_2O)_5CrClCr^{4+}]^{\ddagger} + F^- \quad (6)$$

The substitution of a bridging fluoride by a bridging chloride is an unfavorable reaction, and we conclude that although the reactivity order is $Cl > F$, the stability order of the transition states is $F > Cl$. It is noteworthy that this inner-sphere system displays a behavior entirely analogous to that of the other inner-sphere systems $Co(NH_3)_5X^{2+} + Cr^{2+}$, Fe^{2+}, V^{2+}, and Eu^{2+}, in spite of the fact that the standard free energy change for the exchange reactions is zero.

The exchange reactions between iron(II) and iron(III) catalyzed by fluoride and chloride ions exhibit the inverse reactivity order.[8] It has been shown that part of the $FeCl^{2+}$–Fe^{2+} reaction proceeds *via* an inner-sphere mechanism.[23] For the fluoride-catalyzed reaction, FeF^{2+} has been shown to be the reactive species,[24] and it appears reasonable to assume that an inner-sphere mechanism obtains. The equilibrium constant for reaction 7 calculated from the known rate[25]

$$[FeFFe^{4+}]^{\ddagger} + Cl^- \rightleftharpoons [FeClFe^{4+}]^{\ddagger} + F^- \quad (7)$$

and equilibrium[8] constants is $Q_7 \sim 10^{-5}$. The reaction is unfavorable, and again the transition states exhibit the stability order $F > Cl$. It is noteworthy, as shown above for the reductions of $Co(NH_3)_5X^{2+}$ by europium(II) and iron(II), on one hand, and by chromium(II) and vanadium(II), on the other hand, that there is a reversal in the reactivities of fluoride and chloride complexes in going from the iron to the chromium-exchange systems. However, when one compares the stabilities of the transition states, the two systems conform to the stability order $F > Cl$.

On the basis of the systematization presented above, it seems possible that a comparison of the stabilities of the transition states, rather than the reactivity order for the series F, Cl, Br, and I, could provide a useful indirect criterion for distinguishing between inner- and outer-sphere mechanisms.

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