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First Hydrolysis Constants of Hexaaquacobalt(III) and -manganese(III): Longstanding Issues Resolved

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The acid dissociation constants, K_h, of the hexaaquacobalt(III) and -manganese(III) ions are reported under conditions which minimize the problems of instability of these species at modest acidities (pH 1–4). A rapid and convenient preparation of aqueous Co(III) has been used, and the latter has been reacted with aqueous Mn(II) to form aqueous Mn(III). The noncoordinating buffer H_2PIPPS (1,4-bis(3-sulfopropyl)piperazine) has been used to react with H^+ and provide some control of the pH. Spectrophotometric changes, after stopped-flow mixing for Co(III) and conventional mixing for Mn(III), were used to determine the K_h values. The pK_h values are as follows: Co(III), 3.10 ± 0.07 (6.0 °C) and 2.92 ± 0.04 (20.0 °C) in 1.0 M H^+, Na^+, ClO_4^-; Mn(III), 0.22 ± 0.04 (7.6 °C) and 0.08 ± 0.04 (20.0 °C) in ~4 M H^+, Mn^{2+}, ClO_4^-. Global fits of the data for each metal have been used to estimate the $\Delta H°$ and $\Delta S°$ values for K_h. It is suggested that the unusually high acidity of $Mn(OH_2)_6^{3+}$ may be due to a Jahn–Teller distortion effect.

Introduction

Hexaaquacobalt(III) and -manganese(III) are known to be strong one-electron oxidizing agents. The reactions of these ions were intensively studied in the 1960s and 1970s, but work then and since has left unresolved the value of the hydrolysis constant, K_h, for these ions.

$$M(OH_2)_6^{3+} \overset{K_h}{\rightleftharpoons} M(OH)_5(OH)^{2+} + H^+ \qquad (1)$$

For the first row transition metals, K_h values for aqueous iron(III) and chromium(III) are well established, but scattered results for cobalt(III) leave a wide uncertainty, and the results for manganese(III) appear anomalous. Further studies on the latter two ions no doubt have been inhibited by their tedious and restrictive methods of synthesis. The recent report[1] of a convenient preparation of $Co(OH_2)_6^{3+}$ over a range of concentrations and acidities has removed this restriction. This also provides a convenient route to aqueous Mn(III) through the reaction of the aqueous Co(III) and Mn(II) ions.[2,3]

In most kinetic studies of substitution or electron-transfer reactions involving aqueous Co(III) or Mn(III), the rate law contains a term which has an inverse dependence on the concentration of H^+. This term often is assigned to a reaction with the $M(OH_2)_5(OH)^{2+}$ ion, but the specific rate constant for this pathway can only be calculated if K_h is known. Thus, the specific reactivity of the hydrolyzed aqueous Co(III) and Mn(III) ions remains uncertain.

The unusual feature of the K_h value for $Mn(OH_2)_6^{3+}$ is its large magnitude, with reported values of 5,[4] 0.93,[2] 0.98,[5] 0.96,[6] and 1.0.[7] The $Fe(OH_2)_6^{3+}$ and $Cr(OH_2)_6^{3+}$ ions have K_h values of $\sim 10^{-2.7}$ and $\sim 10^{-4.2}$,[8] respectively, at ambient temperature and modest ionic strengths. Values within this range have been reported for $V(OH_2)_6^{3+}$ (ref 8) and for the later transition metal ions $Ru(OH_2)_6^{3+}$,[9] $Rh(OH_2)_6^{3+}$,[10] and $Ir(OH_2)_6^{3+}$.[11] Therefore, for unknown reasons, $Mn(OH_2)_6^{3+}$ appears to be $\sim 10^3$ times more acidic than the other $M(OH_2)_6^{3+}$ ions.

For Co(III), spectrophotometric studies by Sutcliffe and Weber[12] gave $K_h = 1.7 \times 10^{-2}$ M at 25 °C. But the same

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authors later deemed this value to be suspect due to possible oligomerization. As part of a kinetic study of the reaction of the chloride ion with aqueous Co(III), Sutin and co-workers[13] extracted a K_h value of ~0.2 for $Co(OH_2)_6^{3+}$ from a rather complex rate law. This seemed consistent with the earlier results for $Mn(OH_2)_6^{3+}$. In subsequent kinetic studies in 1968−1970, McAuley and co-workers reported values of 0.1,[14,15] 0.05,[16] and <0.01.[17,18] Davies and Warnqvist[19] suggested an upper limit of $<5 \times 10^{-3}$ M as more consistent with other kinetic studies during the same period,[20,21] and a K_h value of $\sim 10^{-3}$ is sometimes suggested[5,22,23] without any further justification. More recently, Ferrer et al.[24] reported values of $(0.9-1.2) \times 10^{-2}$ M in 1−3 M $LiClO_4$. Few details are given by Ferrer et al., but the conditions (5−6 mM Co(III) and 0.05−0.4 M H^+) were similar to those of the report in 1960 by Sutcliffe and Weber,[12] in which oligomerization was suggested.

In principle, empirical correlations of pK_h values might be used to establish if the published values for Mn(III) are reasonable and to estimate the value for Co(III). Several such correlations have been published based on electronegativities,[25] ionic radii and Slater's screening constants,[26] and ionization potentials.[27] None of these predict the high acidity of $Mn(OH_2)_6^{3+}$, and they seem to be sporadically successful for the corresponding M(III) ions of V(III) through Co(III), so that one cannot be confident of the predictions. There have been several theoretical approaches to estimating pK_h. The results of Li et al.[28] for Mn(III) and Fe(III) were not very encouraging, but Martin et al.[29] were able to calculate the $\Delta G°$ value for the hydrolysis of $Fe(OH_2)_6^{3+}$ to within ~1 kcal mol^{-1} of the experimental value. Rosso and co-workers[30] have noted a correlation between the pK_h value and the calculated energy change for the loss of a proton from a series of $M(OH_2)_6^{3+}$ ions in the gas phase. The correlation is consistent with the high acidity of $Mn(OH_2)_6^{3+}$, but $Co(OH_2)_6^{3+}$ was not treated. Also, a pK_h value of 4.0 instead of 2.6[31] was used for Ga(III), so that neither Ga(III) nor In(III) follow the correlation. Kallies and Meier[32] used their calculated orbital populations for a series of $M(OH_2)_6^{3+}$ ions to rationalize the high acidity of $Mn(OH_2)_6^{3+}$.

To determine K_h, one should observe the system at pH values both above and below the pK_h value. There are several reasons why this is difficult for $Co(OH_2)_6^{3+}$ and $Mn(OH_2)_6^{3+}$. One is oligomerization, the first step of which is illustrated in eq 2.

$$2M(OH_2)_6^{3+} \rightleftarrows (H_2O)_4M(\mu\text{-}OH)_2M(OH_2)_4^{4+} + 2H_3O^+ \quad (2)$$

The product shown is based on the Cr(III)[33] and Fe(III)[34] systems, but it could have a μ-oxo or one μ-hydroxo bridge for other metals. In principle, this complication can be minimized by working at the lowest possible total metal-ion concentration. However, aqueous Co(III) and Mn(III) have further specific chemical problems. The $Co(OH_2)_6^{3+}$ ion oxidizes water.

$$2Co(OH_2)_6^{3+} + H_2O \rightarrow 0.5O_2 + Co(OH_2)_6^{2+} + 2H^+ \quad (3)$$

This reaction becomes too fast for conventional pH titration or standard spectrophotometry of stock solutions at pH > 1.

The $Mn(OH_2)_6^{3+}$ ion undergoes disproportionation.

$$2M(OH_2)_6^{3+} \rightleftarrows Mn(OH)_6^{2+} + Mn(OH_2)_6^{4+} \quad (4)$$

This can be driven to completion by the formation of colloidal and, finally, solid MnO_2.

$$Mn(OH_2)_6^{4+} \rightarrow MnO_2(s) + 4H^+ + 4H_2O \quad (5)$$

These problems can be minimized, but not eliminated, by using the minimum Mn(III) concentration and the maximum possible H^+ concentration and by adding significant amounts of Mn(II).

To achieve pH values in the 2−4 region in the present study, the noncoordinating buffer H_2PIPPS (1,4-bis(3-sulfopropyl)piperazine)[35] has been used both to consume H^+ from the stock solutions of the $M(OH_2)_6^{3+}$ ions and to provide some buffering for the solution. The H_2PIPPS buffer has a pK_a value of 3.7[35] and will provide buffering in the pH 3.1−4.3 range. To overcome the instability of the metal-ion species at pH 2−4, acidic solutions of the metal ion were rapidly mixed with solutions of the buffer immediately before spectrophotometric observation. To use the minimum observable concentrations of the $M(OH_2)_6^{3+}$ ions, the observations have been done mostly in the near-ultraviolet region where the hydrolyzed forms tend to have moderately large molar absorptivity coefficients. It is fortunate that the aqueous M(II) ions, which are inevitably present in the solutions, have quite low absorptivity in this spectral region.

Experimental Section

Materials. A stock solution of iron(III) perchlorate was prepared by dissolving a weighed amount of 99.90% iron wire (Allied Chemical Co.) in ~0.45 M perchloric acid. The solution was treated

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with hydrogen peroxide to ensure complete dissolution and oxidation and then heated on a steam bath to decompose the excess H_2O_2. After cooling, the solution was filtered into a volumetric flask and diluted to the mark. To determine the H^+ concentration, aliquots of this solution were eluted onto Dowex 50W-X8 (H^+ form) cation-exchange resin, which adsorbed the Fe(III), and the eluant was collected and titrated with standard NaOH. The Fe(III) concentration was known from the mass of wire dissolved, and the H^+ concentration was determined by difference. The final concentrations were 9.86×10^{-2} M Fe(III) and 0.125 M H^+.

Small samples of aqueous cobalt(III) perchlorate were routinely prepared by dissolving a weighed amount of $[Co(NH_3)_6][Co(CO_3)_3]$ in the appropriate amount of standardized aqueous $HClO_4$, following the published procedure.[1] The solid $[Co(NH_3)_6](ClO_4)_3$ was separated from the solution by centrifugation, and the solutions were routinely stored in an ice bath for up to 3 h while being used. For the K_h determinations, typical amounts used were 13.3 mg of $[Co(NH_3)_6][Co(CO_3)_3]$ dissolved in 4.00 mL of 1.055 M $HClO_4$. For the preparation of aqueous Mn(III), ~30 mg of solid was treated with 4.50 mL of 1.046 M $HClO_4$. In each case, the final H^+ concentration of the stock was calculated by taking into account the 6 equiv of H^+ that are consumed in the reaction with $[Co(NH_3)_6][Co(CO_3)_3]$.

The buffer, H_2PIPPS, was prepared by the method of Jermyn.[36] The product obtained after filtration and washing with ethanol and ether was found to be the hexahydrate. The anhydrous form can be obtained by heating at 110 °C, but it converts to the dihydrate on exposure to ambient humidity for a few days. The latter was also obtained by drying the hexahydrate over silica gel under vacuum. The 500 MHz ^1H NMR of a 0.011 M solution in D_2O shows peaks at δ 2.187 (m), 2.998 (t), 3.380 (m), and 3.632 (br), similar to the reported spectrum[35] with an unspecified concentration and reference. Anal. Calcd for $C_{10}H_{22}N_2O_6S_2 \cdot 2H_2O$: C, 32.78; N, 7.64; H, 7.15. Found: C, 32.68; N, 7.52; H, 7.22.

The H_2PIPPS buffer prepared as above proved adequate for studies with Fe(III) but showed indications of a coordinating impurity with Co(III) when pH > 2. On mixing with aqueous Co(III), the absorbance showed an exponential increase with a magnitude that increased with increasing H_2PIPPS concentration and with increasing pH. It was suspected that the buffer material contained traces of (3-sulfopropyl)piperazine, and the decision was made to prepare the disodium salt of H_2PIPPS. The crude material from the initial alkylation[36] (~38 g) was stirred in water, and then 8.5 g of NaOH dissolved in 220 mL of ethanol was slowly added to the mixture. When 50% of the ethanol had been added, most of the solid had dissolved, and the solution was filtered before the remainder of the ethanolic NaOH was added. Near the end of the ethanolic NaOH addition, white precipitate began to form. The mixture was cooled at −5 °C for ~2.5 h, and then the product was collected by vacuum filtration, washed with ethanol and ether, and air dried. The product (29.3 g) was dissolved in 55 mL of water, filtered, mixed with 80 mL of ethanol, and cooled and collected as before. This procedure was repeated with the resulting 25.5 g of product, with proportionately scaled down amounts of the solvents to finally yield 23.3 g of product. Potentiometric titration and elemental analysis suggest that this material has 5.7 lattice waters. Anal. Calcd for $C_{10}H_{22}N_2O_6S_2Na_2 \cdot 5.7H_2O$: C, 25.23; N, 5.88; H, 6.65. Found: C, 25.18; N, 5.73; H, 6.67. This material did not show any of the spectrophotometric changes on mixing with aqueous Co(III) that were noted above with H_2PIPPS.

Aqueous Mn(III) has been prepared by the reaction of Mn(II) with MnO_4^-,[37] and it also can be made by the oxidation of Mn(II) with Ce(IV). The former method was always found to leave some residual MnO_2(s), and the Ce(III) from the latter method tends to precipitate at pH > 2. The method used here is based on the earlier observations of Davies[3] and Macartney and Sutin.[5] Solutions of aqueous manganese(III) perchlorate were prepared in situ by the reaction of 0.50 mL aliquots of stock solutions of aqueous cobalt(III) perchlorate with the appropriate amounts of a stock solution of manganese(II) perchlorate. In all cases, the final concentration of Mn(II) was 1.0 M and the Mn(III) concentration was in the range of 0.25−0.6 mM. The manganese(II) perchlorate solution was prepared by the reaction of $MnSO_4 \cdot 2H_2O$ with $Ba(ClO_4)_2 \cdot 3H_2O$ and the removal of $BaSO_4$ by filtration through a 0.2 μm Millipore filter.

Determination of Hydrolysis Constants, K_h. All of these determinations have involved the rapid mixing of a solution of the $M(OH_2)_6^{3+}$ ion in 0.10 M $HClO_4$ with a 0.090 M solution of H_2PIPPS or Na_2PIPPS, adjusted to an appropriate pH (~2−4). Sodium perchlorate was used to adjust the ionic strength when necessary. The absorbance of the mixed solution was measured at several wavelengths, and the pH of the mixed solution was determined.

For $Fe(OH_2)_6^{3+}$ and $Co(OH_2)_6^{3+}$, the mixing was done on a stopped-flow system with a 1.00 cm path length observation cell. The concentration of $Fe(OH_2)_6^{3+}$ was 0.148 mM after mixing with the buffer solution, and the absorbance was determined 20 ms after mixing at 240 and 300 nm using the manufacturer's software. For $Co(OH_2)_6^{3+}$, 1.00 mL of the stock solution described above was added to 24.0 mL of $HClO_4/NaClO_4$ to give a final solution containing 0.10 M $HClO_4$ at the desired ionic strength. The $Co(OH_2)_6^{3+}$ concentration typically was ~0.24 mM after mixing with the buffer solution. Because of the varying stability of the Co(III), the time after mixing at which the absorbance was taken varied from 40 to 5 ms at the highest pH (~4) and temperature (20 °C), and the absorbance was determined at 250 and 270 nm. Under our operating conditions, the absorbance was steady within 2−3 ms after mixing. The $Co(OH_2)_6^{3+}$ concentration was determined from the absorbance at 250 nm after mixing each stock solution with aqueous $NaClO_4$ on the stopped-flow system and by using an extinction coefficient of 3.0×10^3 M^{-1} cm^{-1}. For both systems, six to eight stopped-flow shots were recorded for each sample at each wavelength and the pH of the mixed solution from the stopped-flow system was measured.

For $Mn(OH_2)_6^{3+}$, the stopped-flow system mixing was inconvenient because the solutions form some colloidal MnO_2 during temperature equilibration and data processing. This compromises spectrophotometric measurements and requires repeated cleaning of the instrument. It was found that solutions of Mn(III) containing 1.0 M Mn(II) were stable for the 1−2 min required for a 200 nm wavelength scan on a Cary 214 spectrophotometer. Therefore, the Mn(III) was generated in situ. A solution (12.5 mL) containing 1.0 M manganese(II) perchlorate and perchloric acid, as required in a 5.00 cm path length cylindrical cell, was temperature equilibrated and the spectrum was recorded. Then 0.50 mL of a stock solution of $Co(OH_2)_6^{3+}$ in 1.0 M $HClO_4$ was added, and the solution was mixed and the spectrum recorded. The absorbances at 470 and 300 nm were recorded and corrected for the absorbance of the Mn(II) solution to obtain the absorbance due to the Mn(III) species. The concentration of Mn(III) was determined by adding an aliquot (2.00 or 4.00 mL) of the Mn(III) solution in the cell to 2.50 mL of 1.0 mM aqueous Fe(II) and enough 2.63 M $HClO_4$ to give a final H^+ concentration of ~0.3−0.5 M. Then 5.00 mL of

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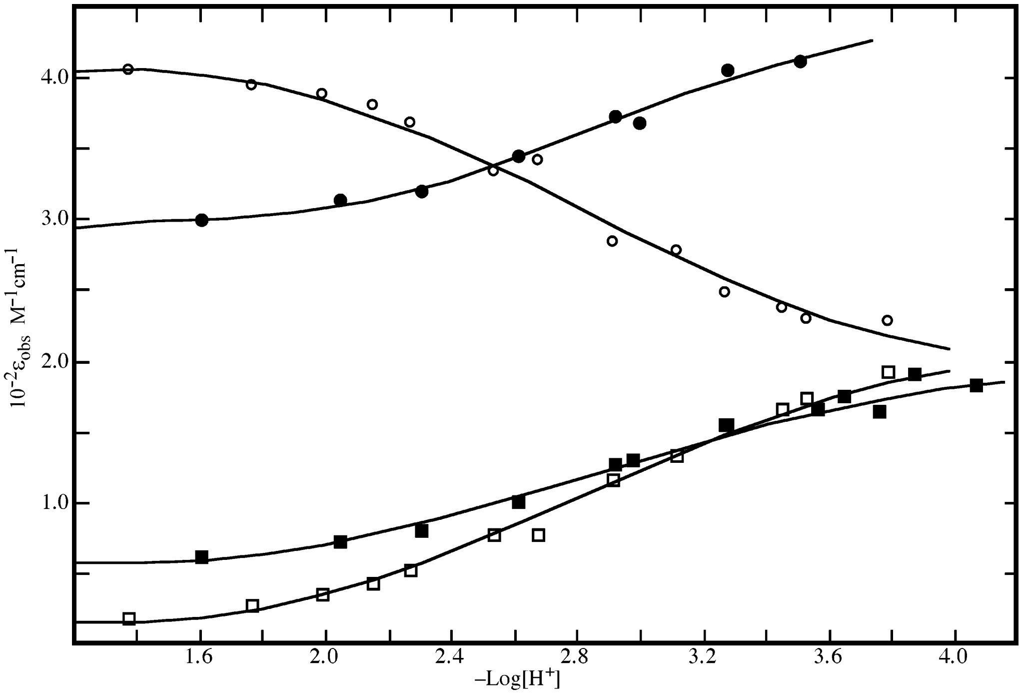

Figure 1. Variation of the molar extinction coefficient, ϵ, with $-\log [H^+]$ in 1.0 M $NaClO_4/HClO_4$ with 0.045 M buffer ($PIPPS^{2-}/HPIPPS^-$) at 20 °C: Fe(III)(aq) at 240 nm (○) and 300 nm (□); Co(III)(aq) at 250 nm (■) and 270 nm (□).

1.50 M aqueous NaSCN was added, and the solution was diluted to 25.0 mL. The absorbance of the Fe(III)-thiocyanate species was determined at 460 nm. Calibration experiments in which the samples contained similar amounts of Mn(II) and Co(II) showed that the absorbance was a linear function of the initial amount of Co(III) added, and gave an extinction coefficient for the analyte of (8.01 ± 0.06) × 10^3 M^{-1} cm^{-1}.

Calculation of K_h. In all cases, the absorbance of the aqueous M(III) ion was determined as a function of pH over the range of acidities necessary to convert $M(OH_2)_6^{3+}$ to >95% $M(OH_2)_5(OH)^{2+}$. The systems were studied at two wavelengths and at least two total concentrations of M(III) ($[M(III)]_{tot}$). At each acidity, the measured absorbances were divided by the $[M(III)]_{tot}$ value and the observation cell path length to obtain the apparent extinction coefficient (ϵ_{obs}). The latter values were fitted to eq 6 by nonlinear least-squares to obtain the best-fit values of K_h and the extinction coefficients of $M(OH_2)_6^{3+}$ and $M(OH_2)_5(OH)^{2+}$, ϵ_H and ϵ_{OH}, respectively.

$$\epsilon_{obs} = \frac{\epsilon_H[H+] + \epsilon_{OH}K_H}{K_H + [H^+]} \tag{6}$$

In the final analysis, the observations at the two wavelengths were fit simultaneously to obtain the overall best-fit parameters.

Instrumentation. An Applied Photophysics SX-17MV stopped-flow system was used with a VWR Scientific refrigerating bath to control the temperature. The Cary 214 spectrophotometer was equipped with a home-built cylindrical cell holder through which thermostated water was circulated from a Colora bath. The pH was measured on a Corning 125 digital pH meter. The conversion of pH to hydrogen ion concentration was done by calibrating the pH meter with appropriate solutions of perchloric acid at concentrations between 0.01 and 10^{-4} M.

Results

The known instability of aqueous Co(III) at pH > 1 required the rapid mixing of moderately acidic solutions of $Co(OH_2)_6^{3+}$ with solutions of $HPIPPS^-$ at various pHs to obtain a pH value in the desired range after mixing on the stopped-flow system. To test this method, the well-studied Fe(III) system was studied first. For these experiments, the ionic strength (μ) is ~0.15 M but varies somewhat with pH as the proportions of H_2PIPPS and $HPIPPS^-$ vary. Least-squares analysis of data at the two wavelengths gives values for pK_h of 3.16 ± 0.04 and 2.77 ± 0.04 at 6 and 20 °C, respectively. These values have the magnitude and temperature dependence expected from earlier studies.[8] The ϵ values are given in Table S1 of the Supporting Information.

To provide a more quantitative comparison to previous results, the $Fe(OH_2)_6^{3+}$ system has been studied in 1.0 M $NaClO_4$ at 20 °C. The pH to H^+ concentration calibration under these conditions allows both the mixed and concentration values of K_h to be determined. The variation of ϵ_{obs} with $-\log [H^+]$ is shown in Figure 1. Least-squares analysis gives the concentration constant as pK_h = 2.88 ± 0.03 and the mixed constant as pK_h = 2.79 ± 0.03. Other fitting parameters are given in the Supporting Information. The former value is in good agreement with earlier studies[8] and with more recent values of 2.72 (25 °C)[38] and 3.03 (10 °C).[39] Therefore, the method of stopped-flow mixing with PIPPS buffer appears to provide reliable values of K_h.

A similar study has been done on the $Co(OH_2)_6^{3+}$ system, except that the instability of aqueous Co(III) required that the stock solution be kept at 0 °C in 1 M $HClO_4$ until just before use. Then this solution was diluted into 0.10 M $HClO_4$, and $NaClO_4$ if required, just before mixing with the PIPPS buffer solution on the stopped-flow system. It was also necessary to adjust the observation times to shorter

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Table 1. Summary of pK_h Values

metal ion	t (°C)	μ (M)[a]	pK_h[b]	pK_h[c]
$Fe(OH_2)_6^{3+}$	6.0	~0.15[d]	3.16 ± 0.04	
$Fe(OH_2)_6^{3+}$	20.0	~0.15[d]	2.77 ± 0.04	
$Fe(OH_2)_6^{3+}$	20.0	1.0	2.79 ± 0.03	2.88 ± 0.03
$Co(OH_2)_6^{3+}$	6.0	1.0	3.00 ± 0.06	3.10 ± 0.07
$Co(OH_2)_6^{3+}$	20.0	1.0	2.83 ± 0.04	2.92 ± 0.04
$Co(OH_2)_6^{3+}$	6.0, 20.0	1.0		2.90[e]
$Mn(OH_2)_6^{3+}$	7.6	~4.0[f]		0.22 ± 0.04
$Mn(OH_2)_6^{3+}$	20.0	~4.0[f]		0.08 ± 0.04
$Mn(OH_2)_6^{3+}$	6.0, 20.0	~4.0[f]		0.12[g]

[a] Ionic strength controlled with Na^+/H^+ClO_4. [b] Mixed constant value based on $[H^+] = 10^{-pH}$. [c] Concentration constant based on $[H^+]$ calculated from the calibration of $[H^+]$ vs pH. [d] Ionic strength varied due to changing ionization state of the buffer. [e] Calculated at 20 °C from a global fit at two wavelengths and two temperatures which gave $\Delta H° = 5.26 \pm 0.77$ kcal mol^{-1} and $\Delta S° = 4.65 \pm 2.6$ cal mol^{-1} K^{-1}. [f] Solutions contain 1.0 M $Mn(ClO_4)_2$ and 0.2−1.2 M $HClO_4$. [g] Calculated at 20 °C from a global fit at two wavelengths and two temperatures which gave $\Delta H° = 2.02 \pm 0.54$ kcal mol^{-1} and $\Delta S° = 6.35 \pm 1.9$ cal mol^{-1} K^{-1}.[40]

values as the pH of the mixed solutions increased. The time was selected to give essentially constant absorbance values during the observation period. Representative results at $\mu = 1.0$ and 20 °C are shown in Table 1. It is apparent from the table that $Co(OH_2)_6^{3+}$ and $Fe(OH_2)_6^{3+}$ have similar K_h values. These results give a concentration constant value of p$K_h = 2.92 \pm 0.04$ and a mixed constant value of p$K_h = 2.83 \pm 0.04$. At 6 °C and $\mu = 1.0$, the concentration constant value is 3.10 ± 0.07 and the mixed constant value is 3.00 ± 0.06. The ϵ values for these data are given in the Supporting Information.

Most kinetic studies with aqueous Co(III) involve a dependence of the rate on the H^+ concentration so that the concentration constants, pK_h, are most relevant to these studies. To analyze this work, it will be useful to have an expression for the temperature dependence of K_h in terms of the normal thermodynamic parameters $\Delta H°$ and $\Delta S°$. To obtain these from the present data at 6 and 20° and $\mu = 1.0$, a global fit of all the data has been done with ϵ_H and ϵ_{OH} at both wavelengths and $\Delta H°$ and $\Delta S°$ as fitting parameters. Only the four ϵ values are needed because the values from the fits at the individual temperatures indicate that ϵ for a particular species is the same, within one standard deviation, at 6 and 20 °C. The values obtained from this analysis are as follows: $\Delta H° = 5.26 \pm 0.77$ kcal mol^{-1}; $\Delta S° = 4.65 \pm 2.6$ cal mol^{-1} K^{-1}; pK_h = 3.10 (6 °C), 2.90 (20 °C), 2.84 (25 °C).[40]

Initial studies with aqueous Mn(III) were based on the premise that previously reported pK_h values were too small and that the acidity of $Mn(OH_2)_6^{3+}$ would be similar to that of $Co(OH_2)_6^{3+}$ and $Fe(OH_2)_6^{3+}$. We were quickly liberated from this presumption when it was observed that mixing 0.30 mM Mn(III) in 0.10 M $HClO_4$ and 1.0 M Mn(II) with 0.09 M $HPIPPS^-$ to give a final pH of ~2 produced a solution that appeared to be fully hydrolyzed. This, in turn, came as something of a relief when it was found that these solutions at pH ~2 were quite unstable with respect to disproportionation and produced MnO_2(s) which foiled repetitive spectrophotometric observations on the stopped-flow instrument. As a consequence of both these observations, the $Mn(OH_2)_6^{3+}$ system has been studied at higher acidities in the range of 0.10 to 3.0 M H^+ by standard spectrophotometry at 300 and 470 nm. This methodology is similar to that of the earlier studies except that the Mn(III) has been generated in situ immediately before observation by the reaction of $Co(OH_2)_6^{3+}$ with $Mn(OH_2)_6^{2+}$. This has allowed the H^+ concentration range to be extended to lower values than previously possible.

The spectrophotometric results for the Mn(III) system at 20 °C are shown in Figure 2. At both 300 and 470 nm, ϵ_{obs} increases with decreasing H^+ concentration and starts to plateau at ~0.1 M. Least-squares analysis of the data at both wavelengths gives $K_h = 0.83 \pm 0.08$ M (pK_h = 0.082) at 20 °C. The tabulated data of Wells and Davies[2] at 300 nm also are plotted in Figure 2. Their ϵ_{obs} values are consistently larger than those found here, possibly due to oligomerization or colloidal MnO_2 in their electrolytically prepared Mn(III) solutions. It also is apparent that they did not observe the plateau region because the data only extend to 0.5 M H^+, and it is something of a mystery as to how they were able to extract a K_h value (0.93) that is close to the value determined here. This system has also been studied at 7.5 °C, and the observations are shown in Figure 2. The data give $K_h = 0.60 \pm 0.06$ M (pK_h = 0.22). It should be noted that the ionic medium in our study is dominated by the 1.0 M $Mn(ClO_4)_2$ and that, in the critical region for pK_h determination, the concentration of $HClO_4$ is in the 0.2 to 1.2 M range. Therefore, the ionic strength varies from ~3.2 to ~4.2 M.

To obtain some quantitative indication of the temperature dependence of K_h, the Mn(III) data was analyzed by the same type of global fit used with Co(III). The values obtained from this analysis are as follows: $\Delta H° = 2.02 \pm 0.54$ kcal mol^{-1}; $\Delta S° = 6.35 \pm 1.9$ cal mol^{-1} K^{-1}; K_h = 0.65 (7.5 °C), 0.75 (20 °C), 0.805 (25 °C).[40] The ϵ values for all of the fits are given in the Supporting Information.

Discussion

The overall conclusion from this study is that the acidity of $Co(OH_2)_6^{3+}$ is not greatly different from that of $Cr(OH_2)_6^{3+}$ and $Fe(OH_2)_6^{3+}$. This is consistent with the earlier assumption of Davies and Warnqvist[19] but not with the most recent experimental determination.[24] On the other hand, $Mn(OH_2)_6^{3+}$ has a K_h value which is ~10^3 times larger than those of the other $M(OH_2)_6^{3+}$ ions, and the value determined here is consistent with several earlier studies.[2,5−7]

The simplest rationale for the unusual K_h value of $Mn(OH_2)_6^{3+}$ would seem to be in terms of the effects of Jahn−Teller distortions of this high-spin d^4 system, as suggested by Kallies and Meier.[32] Their theoretical analysis indicated that, with one electron in the d_{z^2} orbital, only four water ligands would be strong σ-electron donors to the Mn(III), leaving the Mn(III) with a higher electron affinity than expected if all six water ligands were donating equivalently.

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(40) Additional figures are included in the thermodynamic parameters to avoid round-off errors for calculations at other temperatures.

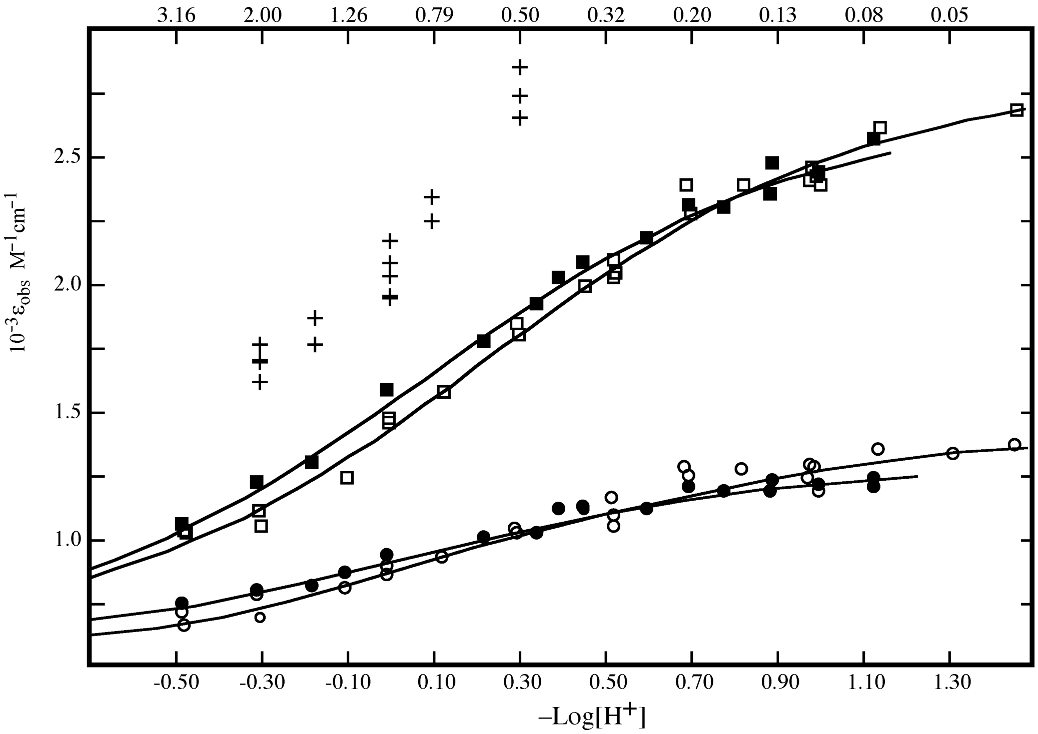

Figure 2. Variation of the molar extinction coefficient, ϵ, with $-\log$ [H^+] (bottom axis) and H^+ concentration (top axis) for solutions of 1.0 M Mn(III)(aq) and varying $HClO_4$ concentrations: 20 °C and 470 nm (●) or 300 nm (■); at 7.5 °C and 470 nm (○) or 300 nm (□).

Table 2. Thermodynamic Data for the Reaction of $M(OH_2)_6^{3+}$ To Form $M(OH_2)_5(OH)^{2+} + H^+$ in Aqueous Perchloric Acid at 25 °C

	V	Cr	Mn	Fe	Co
K_h, M	2×10^{-3} [c]	2.4×10^{-5} [d]	0.8[e]	1.7×10^{-3} [f]	1.4×10^{-3} [e]
$\Delta G°$(rxn)[a]	3.7	5.6	0.13	3.8	3.9
$\Delta H°$(rxn)[a]	10[c]	9.3[d]	2.0[e]	10[f]	5.3[e]
$\Delta S°$(rxn)[b]	21[c]	12[d]	6.4[e]	21[f]	4.7[e]

[a] Units of kcal mol^{-1}. [b] Units of cal mol^{-1} K^{-1}. [c] Furman, S. C.; Garner, C. S. *J. Am. Chem. Soc.* **1950**, *72*, 1785. [d] Xu, F.-C.; Krouse, H. R.; Swaddle, T. W. *Inorg. Chem.* **1985**, *24*, 267. [e] This work. [f] Milburn, R. M. *J. Am. Chem. Soc.* **1957**, *79*, 537.

Then the Mn(III) is presumably more able to polarize the four ligands and to take better advantage of the strong σ-donor ability of the OH^- ligand in the hydrolyzed product. The same electronic effect is not expected for aqueous Cr(III) (t_{2g}^3), Fe(III) ($t_{2g}^3e_g^2$), or Co(III) (t_{2g}^6).

The above rationalization for the high acidity of $Mn(OH_2)_6^{3+}$ is essentially an enthalpy effect and might be expected to produce a more favorable $\Delta H°$ for this hydrolysis reaction. The thermodynamic parameters for the hydrolysis of several M(III) systems are collected in Table 2. Indeed, the $\Delta H°$(rxn) for $Mn(OH_2)_6^{3+}$ is ~8 kcal mol^{-1} less positive than those of its nearest neighbors in the periodic table, $Cr(OH_2)_6^{3+}$ and $Fe(OH_2)_6^{3+}$. The high acidity of $Mn(OH_2)_6^{3+}$ relative to the others is primarily a consequence of the small $\Delta H°$(rxn) which is only partially offset by an ~3 kcal mol^{-1} less favorable $T\Delta S°$(rxn).

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Supporting Information Available: Table S1 of least-squares best-fit parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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